

THE THERMAL PROPERTIES OF FERRIC OXIDE

By
CLIFFORD COOK FURNAS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY IN THE GRADUATE SCHOOL
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HEAT CONDUCTION OF SOLIDS

ABSTRACT

New differential equations representing the laws of heat conduction are derived without making the simplifying assumptions that the thermal conductivity and specific heat are constant. These equations are solved by graphical methods and applied to the determination of thermal conductivities, specific heats, and heats of transition or reaction.

INTRODUCTION

Fourier's analytical treatment of heat flow suggests a method for determining thermal conductivities, specific heats, and heats of transition by one series of measurements, in a centrally heated body. Although this method has been used for the determination of thermal conductivity, it has never been applied in determining the other thermal properties.

That property of matter which Kelvin named diffusivity is dependent upon thermal conductivity, specific heat and density. Arbitrarily the diffusivity, h^2 , of any solid substance, is defined as follows:

$$h^2 = K/CD, \quad (1)$$

where K = thermal conductivity,

C = specific heat,

D = density.

The proposed method involves the determination of the conductivity, K , and the diffusivity, h^2 , which data are used in equation (1) for the computation of the specific heat.

Probably the first suggestion of the use of a centrally heated body for determining conductivity was made in the middle of the nineteenth century by E. Peclet.² He planned to use steam as a source of heat, and to determine the amount of heat flowing by emission formulae, previously determined for the material in question. Later the prevalence and ease of measurement of elec-

trical energy led many investigators to determine heat conductivity by the employment of centrally heated spheres and cylinders in which the energy input might be measured.³⁻¹⁴

Several ingenious methods have been devised for determining h^2 directly. Forbes¹⁵ experimentally determined the diffusivity, h^2 , in a long bar wherein the heat flow was linear. He did not use these data to determine specific heat, C , as he might have done, had he made separate determinations to evaluate the thermal conductivity.

Some of the most accurate determinations of diffusivity have been made by means of a body wherein the temperature varies periodically.¹⁶⁻¹⁹ These methods, however, do not give any means of determining specific heat, because for this computation both thermal conductivity and diffusivity must be known.

THE CENTRALLY HEATED CYLINDER

The only form of apparatus considered will be the cylinder. Although the theory of heat flow in a sphere is simpler, the experimental difficulties are much greater.

Assume a cylinder of solid material, the center axis of which consists of a heating element giving even distribution of heat throughout its length. The cylinder is sufficiently long, or its ends are sufficiently well insulated, so that in a plane parallel to the ends of the cylinder and approximately half way between them, the flow of heat is radial; that is, the flow of heat across this plane is negligible. Means are provided for measuring the temperatures in this plane at various known distances from the center at any time.

The following notation will be employed throughout this discussion:

T = temperature,

t = time,

x, y, z , are space coordinates,

r = radial distance in a cylinder,

A = cross-sectional area of the plane normal to the direction of heat flow,

Q = heat liberated per unit length of the cylinder,

K = thermal conductivity expressed as units of heat transmitted per unit of time per unit of cross-sectional area per unit of length per degree difference in temperature

$$= \frac{\partial Q}{\partial t} \frac{1}{A \left(-\frac{\partial T}{\partial x} \right)},$$

C = specific heat in calories per gram of substance in question,

D = density,

$$h^2 = K/CD. \quad (1)$$

The phenomena of heat conduction are expressed by the Fourier Conduction Equation, which is derived on the assumption that h^2 is a constant. This equation, as usually expressed in rectangular coordinates,^{1, 20, 21, 22} is

$$\frac{\partial T}{\partial t} = h^2 \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right]. \quad (2)$$

For a centrally heated cylinder, using cylindrical polar coordinates, and substituting K/CD for h^2 ,

$$\frac{\partial T}{\partial t} = \frac{K}{CD} \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right]. \quad (3)$$

In the apparatus described, the density, time and temperatures at different radial distances, can be directly measured, leaving two unknowns, K and C , which can be computed if two mutually independent sets of data are available.

The first set of required data is obtained under steady conditions, in which the temperature distribution throughout the cylinder is independent of time and

$$\frac{\partial T}{\partial t} = 0.$$

Under these conditions equation (3) can be integrated,^{4, 5, 7, 23} giving

$$T = a \log_e r + b. \quad (4)$$

By definition

$$K = \frac{\partial Q}{\partial t} \frac{1}{A \left(-\frac{\partial T}{\partial x} \right)}. \quad (5)$$

In the case of a centrally heated cylinder with radial flow

$$K = \frac{\partial Q}{\partial t} \frac{1}{2\pi r \left(-\frac{\partial T}{\partial r} \right)}. \quad (6)$$

If $\partial Q/\partial t$ and K are constant, equations (6) and (4) can be solved simultaneously for K ,^{21, 5, 7, 23} giving

$$K = \frac{\frac{\partial Q}{\partial t} \log_e \frac{r_2}{r_1}}{2\pi(T_1 - T_2)}. \quad (7)$$

Having determined K in this manner, it should be possible to determine C by formal integration of equation (3). This leads to the following solution.²⁴

$$T = \sum a e^{-b^2(K/CD)t} [J_0(br) + L_0(br) \dots].$$

Where

$$J_0(br) = \left[1 - \frac{(br)^2}{2^2} + \frac{(br)^4}{2^2 4^2} - \frac{(br)^6}{2^2 4^2 6^2} \dots \right],$$

and

$$L_0(br) = J_0(br) \log_e (br) + \frac{(br)^2}{2^2} - \frac{(br)^4}{2^2 4^2} \left(\frac{1}{1} + \frac{1}{2} \right) + \frac{(br)^6}{2^2 4^2 6^2} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} \right) \dots$$

Being an infinite series, each term of which is itself an infinite series, this solution has little practical use unless the first term alone of each infinite series is sufficiently accurate. An attempt to use this solution indicated that this is not the case. Even if the solution as outlined were practical, it would be useless for determining the variation of thermal conductivity K and specific heat C , with temperature, because K and C were assumed constant in the derivation of the original differential equations (2 and 3).

TRUE DIFFERENTIAL EQUATIONS

Consider a centrally heated cylinder with radial flow of heat in a central plane normal to the axis. From the definition of thermal conductivity as given in equation (6):

The time rate of heat flow.

$$\frac{\partial Q}{\partial t} = -K 2\pi r \frac{\partial T}{\partial r}.$$

The radial rate of decrease of time rate of heat flow,

$$-\frac{\partial \left(\frac{\partial Q}{\partial t} \right)}{\partial r} = \frac{\partial \left(K 2\pi r \frac{\partial T}{\partial r} \right)}{\partial r}. \quad (8)$$

This equals the time rate of heat absorption at the radius (r)

$$CD2\pi r \frac{\partial T}{\partial t} = \frac{\partial \left(K2\pi r \frac{\partial T}{\partial r} \right)}{\partial r}, \quad (9)$$

$$CD \frac{\partial T}{\partial t} = \frac{\partial T}{\partial r} \frac{\partial K}{\partial r} + \frac{K}{r} \frac{\partial T}{\partial r} + K \frac{\partial^2 T}{\partial r^2}. \quad (10)$$

As K is a function of T alone, in a homogeneous cylinder, dK/dT is a complete differential, and

$$\frac{dK}{dT} \left(\frac{\partial T}{\partial r} \right) = \frac{\partial K}{\partial r}. \quad (11)$$

Substituting for $\partial K/\partial r$ in equation (10)

$$CD \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial r^2} + \frac{K}{r} \frac{\partial T}{\partial r} + \frac{dK}{dT} \left(\frac{\partial T}{\partial r} \right)^2. \quad (12)$$

It will be noted that equation (12) is essentially equation (3), with the addition of one term to make allowance for the change in K with temperature. Provided equation (12) is used in the differential form, no implication is made that either C or D is constant.

Certain advantages are evident when using temperature as a function of the logarithm of the radius. Equation (12) may be developed in terms of $\log_e r$ instead of r by substituting $d \log_e r$ for dr/r in equation (9).

$$CD \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial \left(K \frac{r \partial T}{\partial r} \right)}{\partial r} = \frac{1}{r^2} \frac{\partial \left(K \frac{\partial T}{\partial \log_e r} \right)}{\partial \log_e r},$$

$$CD \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{dK}{d \log_e r} \frac{\partial T}{\partial \log_e r} + \frac{K}{r^2} \frac{\partial^2 T}{\partial \log_e r^2}.$$

From equation (11) and $dr = r d \log_e r$

$$CD \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{dK}{dT} \left(\frac{\partial T}{\partial \log_e r} \right)^2 + \frac{K}{r^2} \frac{\partial^2 T}{\partial \log_e r^2}, \quad (13)$$

$$CD \frac{\partial T}{\partial t} = \frac{1}{(2.303)^2 r^2} \left[\frac{dK}{dT} \left(\frac{\partial T}{\partial \log_{10} r} \right)^2 + K \left(\frac{\partial^2 T}{\partial \log_{10} r^2} \right) \right]. \quad (14)$$

Equation (14) is simpler than equation (12) in that it has one less term. Later equation (14) will be shown to possess other particular advantages in graphical solutions. Under some conditions it may be of advantage to use the relation of $\log_e T$ and $\log_e r$. The equation corresponding to equations (12) and (14) is,

$$CD \frac{\partial T}{\partial t} = \frac{KT}{(2.303)r^2} \frac{\partial^2 \log_{10} T}{\partial \log_{10} r^2} + \frac{KT}{r^2} \left(\frac{\partial \log_{10} T}{\partial \log_{10} r} \right)^2 + \frac{T^2}{r^2} \left(\frac{\partial \log_{10} T}{\partial \log_{10} r} \right)^2 \frac{dK}{dT} \quad (15)$$

It is worth noting that in equations (12), (13), (14), and (15) the absolute value of r as measured from the exact center of the cylinder must be used, because r or $\log r$ enters into the equation. Neither r nor $d \log r$ is independent of the integral value of r . In equation (15) it is equally necessary that the absolute value of temperature be used for the same reason.

The solution of equations (12), (14), or (15) by formal integration appears even more impractical than the solution of the simpler equation (3). However, sufficient data may be obtained to determine graphically the values of the derivatives in these equations. This method should lead to a satisfactory solution of the equations if the experimental data can be obtained with sufficient accuracy.

SOLUTION OF THE TRUE DIFFERENTIAL EQUATIONS BY MEANS OF GRAPHICAL DIFFERENTIATION

As has been indicated, the solution of these equations requires two independent sets of data:

1. For Steady States, giving the corresponding values of temperature, T , and radial distance, r , when T is independent of time, t , and $\partial Q/\partial t$ is a constant, from which the conductivity K is obtained by means of equation (6), or, if the thermal conductivity K is a straight line function of temperature, the average conductivity, K_a , over a small temperature range is equal to that at the average or mean temperature of the range taken, and may be computed by using equation (7).

2. For States not Steady, giving the corresponding values of temperature, T , and time, t , at particular radial distances.

The method of graphical solution is best explained by an example. For this purpose actual data will be used for illustration.

GRAPHICAL SOLUTION FOR THERMAL CONDUCTIVITY, K

Temperature data obtained during a steady state are plotted as the curve " T " in Fig. 1, as a function of the radius r . If $\partial T/\partial r$ can be evaluated as a function of r , equation (6) may be solved for conductivity, K , provided dQ/dt is known.

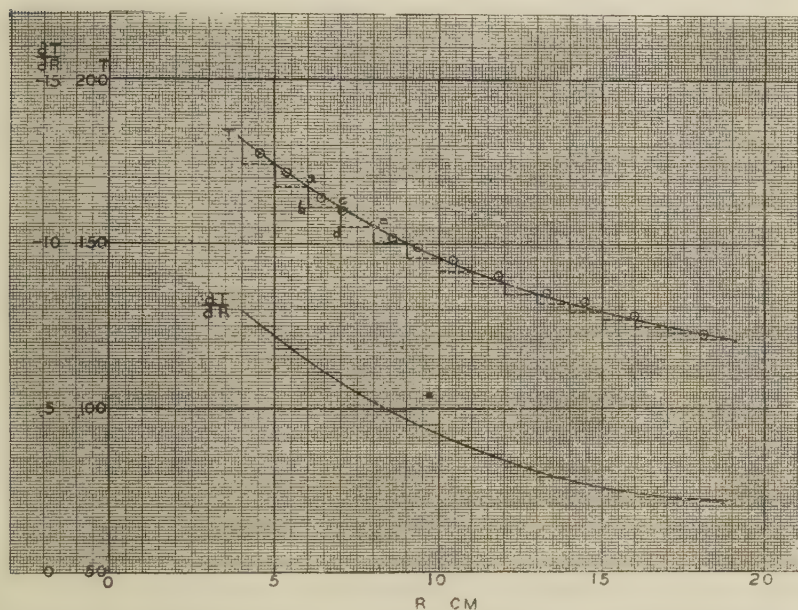


FIG. 1

The heat supplied in the center per unit length of the cylinder per unit time, $(\partial Q/\partial t)$, is readily computed if electrical energy is used for heating.

Graphical differentiation²⁵ of the curve " T " of Fig. 1 is accomplished by drawing ordinates to the curve at intervals along the abscissa. The abscissæ are drawn from each intersection of the ordinate with the curve, to the next preceding ordinate, as lines bc , de , etc.

Then $ab/bc = \Delta T/\Delta r$.

The increment in T , ΔT , must equal the area under the derived curve, for the corresponding increment in r , Δr .

Erecting rectangles on the abscissa with a base of Δr and having areas numerically equal to the corresponding ΔT for the " T " curve, the ordinate of the rectangle is equal to $\Delta T/\Delta r$.

By drawing a smooth curve through the tops of the rectangles in such a manner that the areas above the top of the rectangle and below the line are approximately equal to the corresponding areas above the line, the curve is a very close approximation to the derivative of T with respect to r .

The value of $\partial T/\partial r$ for any given r can then be directly read from the curve " $\partial T/\partial r$ " in Fig. 1, and K can be evaluated from equation (6) as indicated.

$$\text{Since } d \ln r = \frac{dr}{r},$$

$$K = \frac{\frac{\partial Q}{\partial t}}{\frac{2}{2.303} \left(- \frac{dT}{d \log_{10} r} \right)}. \quad (16)$$

As $\partial Q/\partial t$ is constant for a steady state $dT/(d \log r)$ must be constant if K is constant. Under these conditions the curve of T plotted against $\log r$ must be a straight line. As this is approximately true, the T against $\log r$ curve changes its slope only slightly and is easier to differentiate accurately than that of T against r which changes its slope very rapidly as r becomes small. This is the most important advantage obtained in using the function of the logarithm of r .

GRAPHICAL SOLUTION FOR SPECIFIC HEAT

Figure 2 is a plot of actual time-temperature data obtained in an unsteady state.

The values of temperature at constant time such as $\frac{1}{2}$ hour as at A in Fig. 2 are plotted against the corresponding radii, as the curve " T " in Fig. 3. This curve, graphically differentiated as previously explained, gives the first derived curve " $\partial T/\partial r$." The latter curve is differentiated in the same manner, giving the second derived curve " $\partial^2 T/\partial r^2$."

All the quantities on the right hand side of equation (12) have now been obtained except dK/dT . This differential coefficient is easily evaluated from the data for K at various temperatures which have been obtained from the steady states, and is generally a constant for homogeneous solids. Each of the time-temperature curves in Fig. 2 must be graphically differentiated in the region in which they are to be used. When this has been done, all of the data are at

hand for the evaluation of CD at the various temperatures represented by points $a_1, a_2, a_3, a_4, \dots$ in Fig. 2.

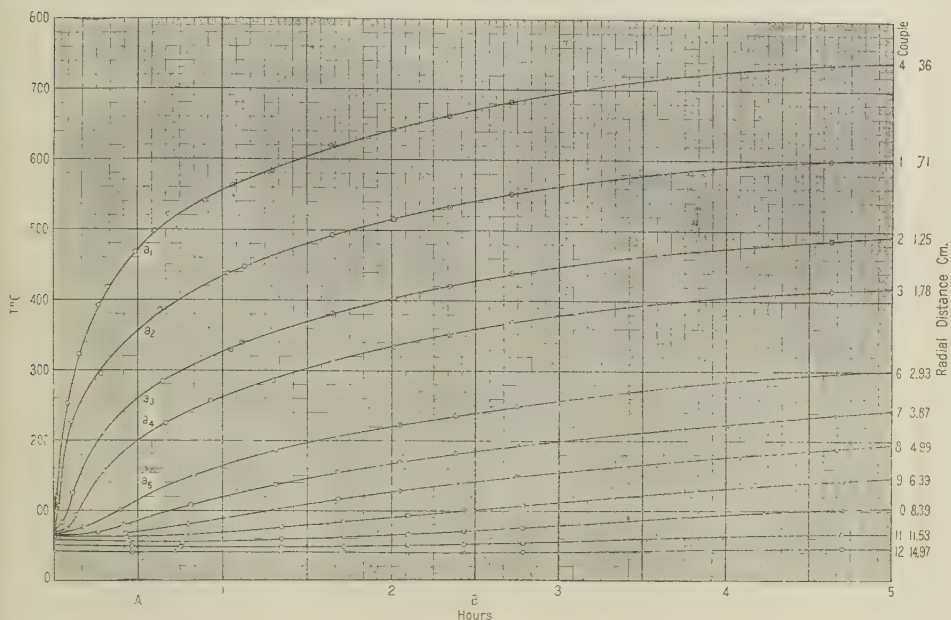


FIG. 2

If CD is to be evaluated at point a_2 (Fig. 2) the values of $\partial^2 T / \partial r^2$ and $\partial T / \partial r$ are taken from Fig. 3 at point where $r = r_2$. The value of $\partial T / \partial t$ is taken from the derived curve of curve r_2 in Fig. 2 at point A . Values of K , r , D , and dK/dT are substituted in equation 12 and C evaluated.

The T -log r curves or the log T -log r curves are usually much easier to differentiate, and for this reason generally preferable to the T - r curves. The principle of solution is exactly the same as in the case of the T - r curves, the substitution being in equation (14) or (15) instead of in equation (12).

ALTERNATIVE METHOD FOR COMPUTING SPECIFIC HEAT, INVOLVING GRAPHICAL INTEGRATION

This method determines the average specific heat C_a over a small temperature range in a thin cylindrical section, between the radial distances r_1 and r_2 , by graphical summation, or integration,

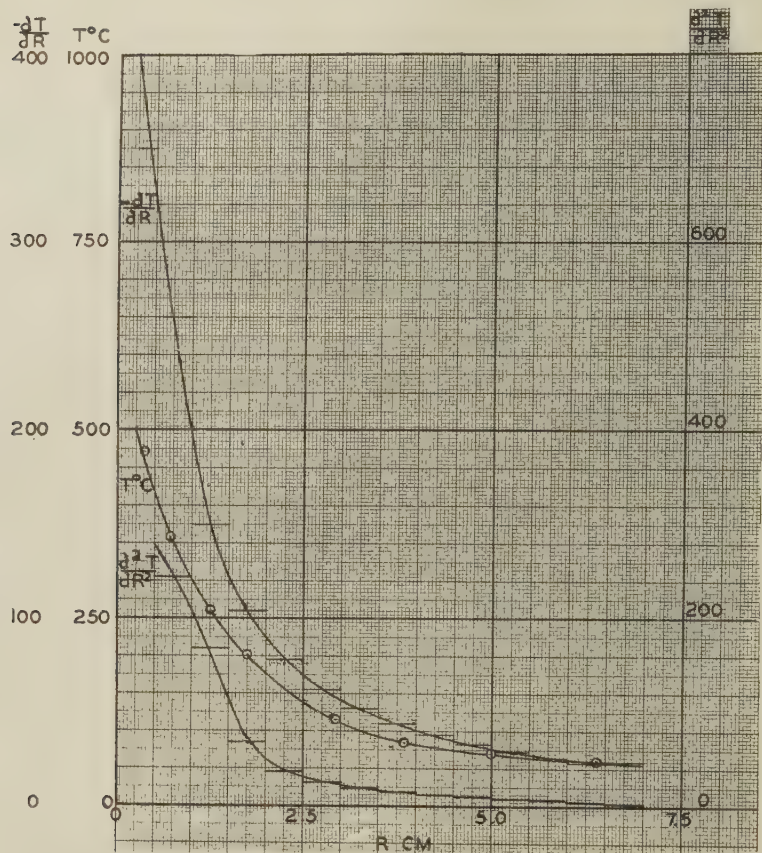


FIG. 3. Section A, Run 1

of the heat quantities flowing into and out of this section during a time interval t_1 to t_2 .

From equations (6) and (16) the rate of heat flow, or quantity of heat flowing per unit of time, across the cylindrical area at r is

$$\frac{\partial Q}{\partial t} = K2\pi r \left(-\frac{\partial T}{\partial r} \right) = K2\pi \left(-\frac{\partial T}{\partial \log_e r} \right). \quad (17)$$

This equation may be applied to the heat quantities flowing into the thin section at r_1 and out of the section at r_2 . The difference between these quantities is equal to the heat absorbed in the thin section per unit of time. By integrating equation (17) for the heat

flowing into the section at r_1 during the time interval t_1 to t_2 , and for the heat flowing out of the section at r_2 during the same time interval, the heat absorbed by the section during this time interval may be obtained by subtracting the latter integral from the former.

The heat absorbed

$$\begin{aligned} &= \int_{t_1}^{t_2} K 2\pi r_1 \left(-\frac{\partial T}{\partial r} \right) dt - \int_{t_1}^{t_2} K 2\pi r_2 \left(-\frac{\partial T}{\partial r} \right) dt \\ &= \int_{t_1}^{t_2} K 2\pi \left(-\frac{\partial T}{\partial \log_e r} \right) dt - \int_{t_1}^{t_2} K 2\pi \left(-\frac{\partial T}{\partial \log_e r} \right) dt. \end{aligned} \quad (18)$$

In order to make this integration, K and $[-(\partial T/\partial r)]$ or $[-(\partial T/\partial \log_e r)]$ must be known as a function of time, t . As K is known as a function of temperature, and Fig. 2 gives the relationship between temperature and time, K can be readily computed as a function of time. $[-(\partial T/\partial r)]$ or $[-(\partial T/\partial \log_e r)]$ can be computed for various values of r and time, t , by the method illustrated in Fig. 3. As formal equations for these relations are not easily obtainable, graphical integration of equation (18) offers the most convenient method of solution.

If two curves representing $K 2\pi [-(\partial T/\partial \log_e r)]$ at r_1 and $K 2\pi [-(\partial T/\partial \log_e r)]$ at r_2 are plotted using t as the abscissa, the value of the difference of the integrals in equation 18 is equal to the area between the curves. It might be noted that, if these curves be plotted from data obtained in a steady state, theoretically they will coincide, thereby offering a means of checking the accuracy of thermal conductivity data obtained during the steady state.

The sensible heat absorbed per unit volume of material is

$$\int_{T_1}^{T_2} CDdT.$$

The volume of the thin cylindrical section of unit length is

$$\int_{r_2}^{r_1} 2\pi r dr.$$

Therefore, the sensible heat absorbed

$$= 2\pi D \int_{r_1}^{r_2} r dr \int_{T_1}^{T_2} C dT. \quad (19)$$

If the specific heat is considered constant over the temperature range $T_2 - T_1$, equation (19) becomes

Sensible heat absorbed

$$= 2\pi C_a D \int_{r_1}^{r_2} r(T_2 - T_1) dr. \quad (20)$$

As $T_2 - T_1$ is itself a variable depending upon the radius, r , the integral expression of equation (20) cannot be evaluated unless $(T_2 - T_1)$ is known as a function of r .

This can be obtained from curves similar to the T curves of Fig. 3 for time t_1 and t_2 . The values for $(T_2 - T_1)$ for any particular radius during the time interval $t_2 - t_1$ represented by the two curves, is the difference between the ordinates of the two curves. These data allow values for $r(T_2 - T_1)$ to be plotted as a function of r as abscissa.

The area under this curve, between r_1 and r_2 , will be numerically equal to the value of the integral in equation (20). Then the equation

$$C_a = \frac{\text{Sensible Heat Absorbed}}{2\pi D \int_{r_1}^{r_2} r(T_2 - T_1) dr} \quad (21)$$

can be solved for C_a .

This method does not involve a second derivative which may be troublesome and inaccurate, unless special precautions are taken, and accordingly offers some advantages over the previous method which involved a second derivative. By considering sections through which the temperature drop is small, the specific heat may be obtained by the latter method with a degree of accuracy equal to that obtained by the derivative method.

APPLICATION TO DETERMINING HEATS OF TRANSITION

The total heat absorbed, as computed by equation (18), includes all sensible heat and any other possible heat quantities such as may be involved in any allotropic transformation. If the specific heat of the material has been computed by any method, the sensible heat absorbed may be determined by equation (19), as has been indicated. The heat of transformation is equal to the total heat absorbed as computed from equation (18), less the sensible heat absorbed as computed by equation (19).

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THERMAL PROPERTIES OF FERRIC OXIDE

ABSTRACT

The known specific heat of crystalline Fe_2O_3 is extended from 100°C . to 650°C . A new allotropic transformation at 360°C . is reported, and the heat absorbed at this transition is reported as 4.85 calories per gram. The total heat absorbed for all transitions between 650°C and 825°C . is estimated at 41.8 calories per gram.

The thermal data of the oxides of iron are very incomplete. There are no data on the specific heat of ferric oxide above 100°C . Table I is believed to be a complete compilation of all the important determinations of the specific heats of the three common iron oxides.

TABLE I

Substance.	Specific Heat.	Temperature $^\circ \text{C}$.	Reference.
Hematite.....	0.1645	15 to 99	Oeberg ²⁶
Hematite.....	0.1680	12 to 100	Joly ²⁷
Hematite.....	0.1742	16 to 95	Abt ²⁸
Fe_2O_3	0.0730	- 192 to - 81	Russel ²⁹
Fe_2O_3	0.1320	- 74 to 0	Russel
Fe_2O_3	0.1600	44 to 3.5	Russel
Fe_2O_3	0.1680	13 to 97	Regnault ³⁰
Fe_2O_3	0.0412	- 185	Parks and Kelley ³⁴
Fe_2O_3	0.0858	- 123	Parks and Kelley
Fe_2O_3	0.1162	- 75	Parks and Kelley
Fe_2O_3	0.1561	16	Parks and Kelley
Magnetite.....	0.1560	18 to 45	Kopp ³¹
Magnetite.....	0.1680	24 to 99	Weiss and Beck ³²
Magnetite.....	0.2300	400	Weiss and Beck
Magnetite.....	0.2800	580	Weiss and Beck
	Transformation Point		
Magnetite.....	0.2300	580	Weiss and Beck
Magnetite.....	0.2600	750	Weiss and Beck
Magnetite.....	0.0488	- 173	Parks and Kelley ³⁴
Magnetite.....	0.0968	- 120	Parks and Kelley
Magnetite.....	0.1205	- 76	Parks and Kelley
Magnetite.....	0.1570	22	Parks and Kelley
Fe_3O_4	0.1680	(32 to 212 $^\circ \text{F}$.)	Marks ³³
Fe_3O_4	0.1678	24 to 99	Regnault ³⁰

This paper reports the results of a series of determinations of the specific heat of finely powdered, crystalline ferric oxide, by means of a centrally heated cylinder of the powder by the method discussed in the previous paper (Heat Conduction of Solids).

PREPARATION OF SAMPLE OF FERRIC OXIDE

One thousand pounds of roll scale were obtained through the courtesy of the Illinois Steel Company of Gary and the Bourne Fuller Steel Company of Cleveland. The method found best for preparing ferric oxide from this material is described below.

The material was crushed between steel rolls and then ground to pass 100 mesh in flint pebble ball mills. The finely ground material was placed in a gas-fired reverberatory furnace and maintained at a temperature of 900° C. to 1000° C. in an oxidizing atmosphere, for a period of about ten hours. This treatment oxidized practically all of the iron to the ferric state, and eliminated most of the carbon and sulfur. The calcined oxide was screened through 100 mesh. The final product consisted of about 500 pounds of finely divided crystalline oxide, an average sample of which gave the following analysis.

Fe ₃ O ₄ ³⁵	0.117%
Fe ₂ O ₃ ³⁶	98.730%
Metallic iron ³⁷	0.000%
SiO ₂ ³⁸	0.620%
S ³⁹	0.027%
P ⁴⁰	0.020%
Mn ⁴¹	0.345%
C	0.028%
Loss on Ignition	0.087%
Total	99.974%

As it is very important that the powder should be of uniform density throughout the cylinder, considerable pains were taken to insure uniform tamping of the powder. After considerable practice the error of tamping became quite small. The final determination of apparent density was made by three trials in a two liter graduated cylinder. The average apparent density was found to be 2.79 grams per cubic centimeter, with a maximum variation of 0.72 per cent.

The true density was determined by means of a volumeter, using kerosene as the liquid for displacement. The average of three determinations was found to be 4.35 grams per cubic centimeter,

with a maximum variation of 4.12 per cent. The accuracy of this determination is much less than for the apparent density. As the apparent density rather than the true density is used in making all calculations, the errors in the true density are unimportant.

CONSTRUCTION OF APPARATUS

The dissociation pressure of ferric oxide is quite appreciable at relatively low temperatures, and amounts to approximately 0.2 of an atmosphere between 1000°C. and 1100°C. , increasing to 1

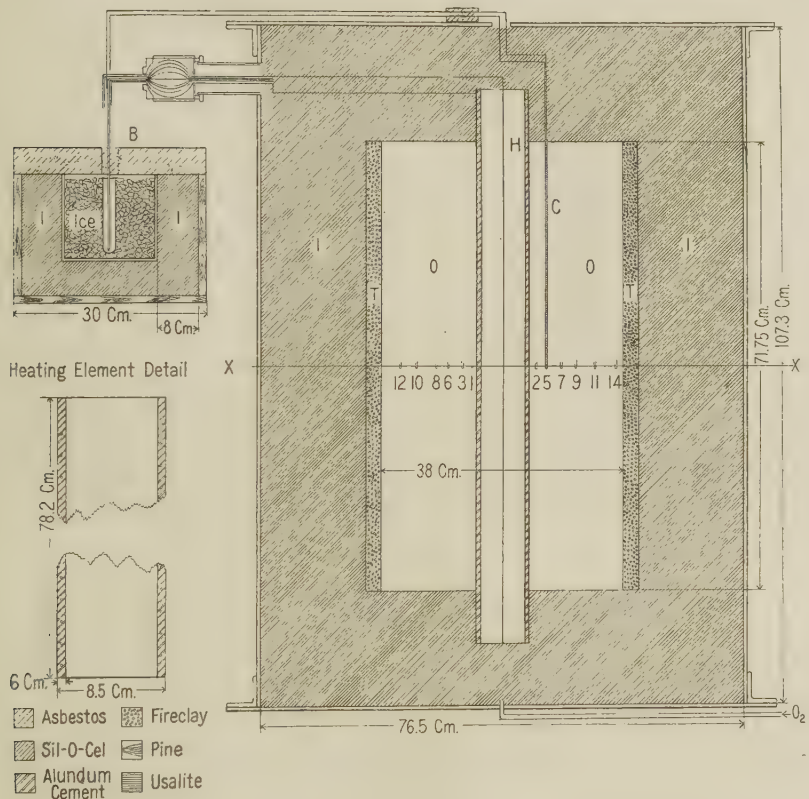


FIG. 4

atmosphere at 1300°C. ⁴² For this reason the cylinder of oxide must be enclosed in a gastight drum in which the atmosphere can be controlled.

The apparatus is shown in cross-section in Fig. 4. The drum is

welded from sheet steel about $3/32$ inch thick. The top and bottom plates are bolted to flanges of angle iron welded to the drum. Each plate is braced with four angle irons and bolted down.

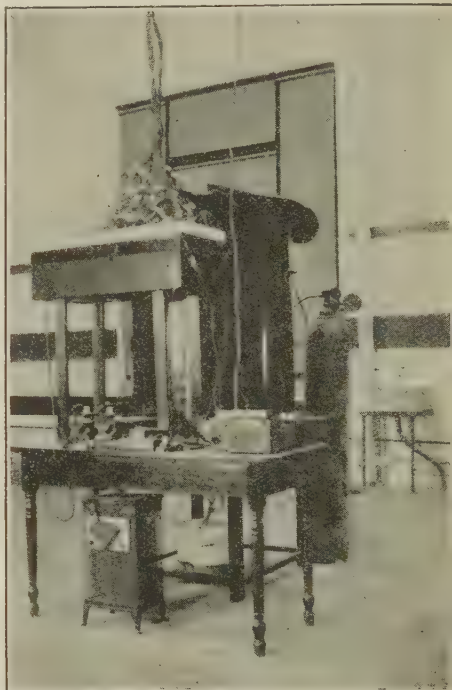
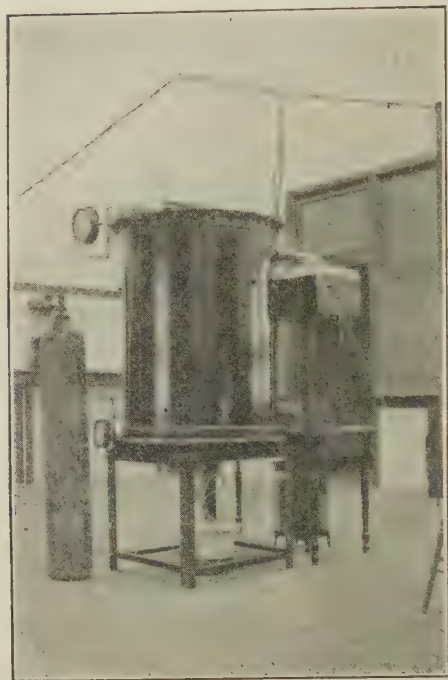


FIG. 5. Thermal Properties of Ferric Oxide

The cylinder of ferric oxide, *O*, was formed by tamping the material into a fireclay thimble, *T*. In the final arrangement of the apparatus the cylinder was centrally traversed by the heating element, made of chromel A wire No. 14, wound in the form of a helix with a diameter of 8 cm. and a pitch of 1.7 cm., covered with alundum cement. The cylinder of oxide was entirely surrounded by Sil-O-Cel for thermal insulation.

All temperatures were measured by means of thermocouples. Four Platinum, Platinum-Rhodium couples were used in the central portion, eight Chromel P, Alumel couples were used in the outer portion of the cylinder, and one Copper-Constantan couple was used to measure the temperature of the cold junction box of the noble metal couples.

The couples were carefully and individually calibrated. All couples of the same type were made from the same wire stock and have therefore practically the same calibration.

One of the most serious difficulties encountered in measuring physical quantities lies in the fact that the presence of measuring instruments usually alters the quantity to be measured. Every effort should be made to keep this alteration down to a minimum. In the present work all thermocouples or protection tubes placed in the oxide are foreign material and hence tend to alter the temperature from the value which it would have if the foreign matter were not present.

In order to keep foreign material to a minimum, protection tubes of the smallest possible size of Usalite, made by the Stupakoff Laboratories were used. This consideration is particularly important in the inner part of the cylinder, because the amount of foreign material is proportionally greater, due to the smaller radius.

After considerable experimentation in protecting the noble metal couples, the ends of the two hole Usalite protection tubes were slitted by means of small carborundum dental separating disks and the bead of the couple pulled into the slit. The slit was then filled with green pyrometer tube body clay, dried, and baked in an oxy-gas flame. Another bit of clay was then forced into the end to fill shrinkage cracks, and baked. This method gave a nice fitting plug over the end of the couple. A coat of spark plug glaze, obtained from the Champion Porcelain Company, was then applied, carefully dried, and fused in an oxy-gas flame, then annealed over a Meker burner. A second coat of glaze was then applied in the same manner. The temperature of fusion of the glaze was sufficiently low that the platinum did not melt. This glaze, however, will withstand temperatures up to 1300° C. As this method gave a very satisfactory protection on the end, with practically no increase in the diameter of the tube, it was possible to have protected thermocouples with an outside diameter of 0.35 cm., or about one-third that of an ordinary lead pencil.

As it is less important that the couples situated farther from the center should be of such small diameter, a simpler method was used for protecting the base metal couples. One of the wires was strung with 5 cm. sections of Usalite one hole tubing, $1.5 \times .75$ mm., and both wires inserted into a larger Usalite tube, 3.75×2.75 mm., the end of which had previously been closed by fusing. These tubes

were quite satisfactory, and were only slightly larger than those used for the noble metal couples.

All couples were carefully calibrated by the standard method of comparison. The standard of comparison was Bureau of Standards Couple No. 2306, a Platinum, Platinum-Rhodium couple standardized by the Bureau of Standards during the summer of 1925.

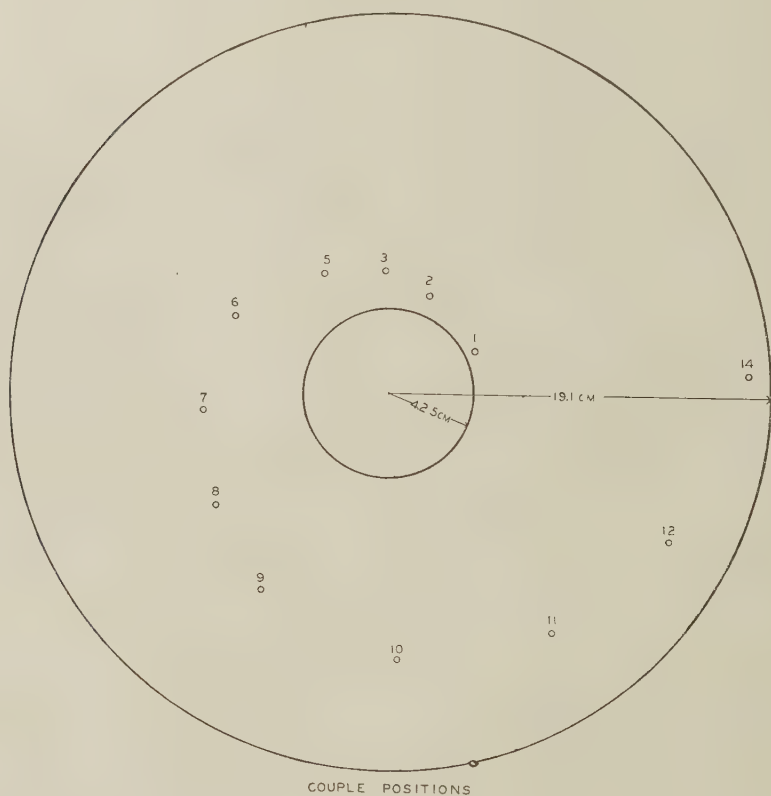


FIG. 6

The ideal spacing of couples in the cylinder of oxide would be that arrangement which would give the same temperature difference between any two adjacent couples. As equation (4)

$$T = a \log r + b$$

is approximately true at the steady state, equal differences in the logarithm of r should give equal differences in T .

The thermocouples were placed during the formation of the ferric oxide cylinder when the depth of oxide was 35.9 cm. This was accomplished by taking a straight, pointed iron rod 2.5 mm. in diameter and making a hole in the oxide to a depth of 5 cm. Extreme care was taken to keep the rod parallel to the heating element. The oxide was sufficiently well packed so that when the rod was withdrawn the oxide did not cave in. The couple was then pushed into the hole to a depth of 5 cm., care being taken to keep the couple parallel to the heating element.

In order to keep from massing the foreign material in one sector of the oxide the couples were spaced 30 to 60 degrees apart, in the form of a logarithmic spiral in the middle plane, as shown in Fig. 6. In measuring the couple distances sharp dividers were used to measure the inside distance between the couple and the heating element, and outside calipers were used to measure the outside distances between the two. An average of three readings was taken, as given in Table II. The bead of the couple was assumed to be in the center of the protection tube.

TABLE II

DISTANCE OF THERMOCOUPLES FROM CENTER OF CYLINDER IN CENTIMETERS

Couple No.	Average.	Couple No.	Average.
1.....	4.83	8.....	10.34
2.....	5.30	9.....	11.87
3.....	6.24	10.....	13.50
5.....	6.87	11.....	14.66
6.....	8.59	12.....	15.92
7.....	9.38	14.....	18.00

The cold junctions of the noble metal couples were assembled in the cold junction box, *J*, Fig. 4, on the top of the drum. The temperature of this junction box was recorded by a copper-constantan couple. The cold junctions of all base metal couples were placed in test-tubes sealed with paraffin and kept in melting chipped ice in a refrigerator, *B*.

All thermocouple and power leads were individually wrapped with graphite valve packing and brought through stuffing boxes in order to make the drum gastight. Where the leads passed through Sil-O-Cel they were protected by asbestos tubing.

Figure 7 is a diagram of the power, thermocouple, and measuring circuits.

Direct current of constant voltage is essential as the source of power for this experiment. Direct current must be used because of the possibility of hysteresis loss in the body of the oxide and consequent unequal power distribution if alternating current were used, and because of the difficulty of making accurate measurements

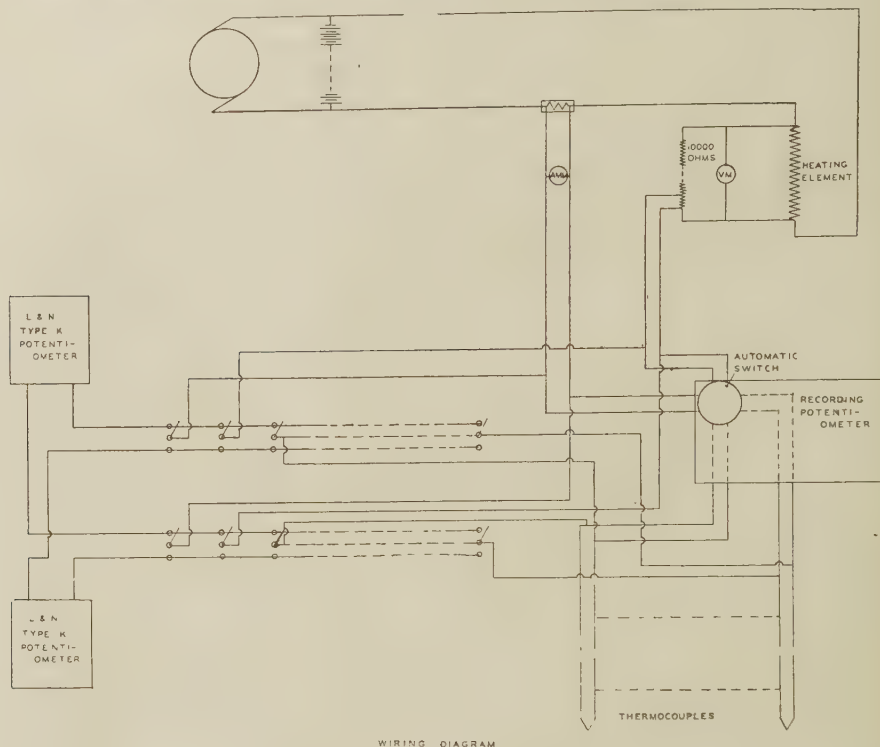


FIG. 7

of alternating current. A motor generator set was used as the source of power, with a battery of lead storage cells floating on the line, parallel to the heating circuit. Under ordinary circumstances this gave a voltage regulation of $\frac{1}{4}$ to $\frac{1}{2}$ per cent.

Two types of instruments were used to measure temperatures and power input. In order to have a continuous record of the behavior of the apparatus, a Leeds and Northrup 12 point, recording potentiometer was used. The guaranteed accuracy of this instrument is 0.1 millivolt, but by careful adjustment it was found to be

very dependable to 0.02 millivolt. For the sake of greater accuracy additional measuring circuits were run to a specially constructed switchboard which enabled any circuit to be independently connected at any time to either of two Leeds and Northrup Type K potentiometers with precision galvanometers. It was thus possible for two observers to work simultaneously at taking readings. The accuracy of these instruments is 0.0001 millivolt.

Twelve of these circuits were of course in parallel with those of the recorder, but since the recorder was in contact with one particular circuit only 1/12 of the time, the two measuring circuits did not interfere with each other.

The recording galvanometer operates accurately with an external resistance up to 40 ohms. As in no case did the external resistance exceed 3 ohms, the lag due to lead resistance introduced no error.

The source of working current for all potentiometers was isolated storage cells. Leeds and Northrup Weston Standard Cells were used for adjusting the potentiometers.

Heating current was measured by means of 50 millivolt current shunts of 10 and 50 ampere capacity. Leads from the shunts were connected to a millivoltmeter and to the potentiometer measuring circuits.

The voltage of the heating current was measured directly by a voltmeter and also by means of the potentiometers in conjunction with a volt box. The volt box gave voltage ratios up to 10,000/1.

The arrangement and dimensions of the apparatus just described were developed after other and less satisfactory arrangements had been tried. It was found, as is to be expected, that any longitudinal flow of heat gives values of thermal conductivity at different radii but at the same temperature, which are inconsistent. If the diameter of the heating element is small, the cross-sectional area of the conducting medium ($2\pi r \times \text{length of the cylinder}$) is small, and the temperature gradient, $(\partial T/\partial r)$, through that part of the cylinder having a small radius will be proportionally large. Likewise, if the cylinder is poorly insulated, a large amount of heat must be forced through the cylinder to maintain the desired higher temperature, causing a still larger temperature gradient, $(\partial T/\partial r)$. As the first and second derivatives of temperature with respect to radius ($\partial T/\partial r$, $\partial^2 T/\partial r^2$) are of opposite sign, and enter as an algebraic sum in the equation (equation 12,) it is essential that they be as small as

possible to eliminate the inaccuracy inherent in a small difference between two large numbers. These sources of error were encountered in the earlier trials and largely eliminated in the arrangement of apparatus described, by using very complete insulation, 17 cm. (6 inches) of Sil-O-Cel around the cylinder of iron oxide, and a relatively large heating element, $8\frac{1}{2}$ cm. ($3\frac{1}{4}$ inches) in diameter.

OPERATION

The oxide cylinder and insulation were dried by heating with electric power through the central coil until the outside of the oxide was well over 150°C . for over a week. The power input was then maintained at 200 watts for another week until the first steady state (*L*) was reached.

The second steady state (*M*) was obtained by allowing the furnace to cool for three days and then bringing it to equilibrium with a power input of about 80 watts. Eleven days elapsed before the temperatures became steady.

In the next run the power input was started at 1,250 watts to send a relatively intense heat wave through the oxide. The power was gradually decreased as the oxide came up to the desired temperature, until a steady state (*N*) consuming about 350 watts was reached. By using this method of over-heating the interior equilibrium was attained in six days. At this time the temperature of the inside couple was 650°C . Time-temperature data were taken by the type K potentiometer during all rapid rises in temperature. The 12 point potentiometer recorder was used at all times, but was not sufficiently accurate to give quantitative data of the heat waves.

Operating difficulties began above 700°C ., due to condensation of moisture in the outer layers of Sil-O-Cel. A temporary short circuit developed in the heating element. Soon after the short circuit developed the inside thermocouple began to give absurd results. Time-temperature data up to about 1000°C . was obtained without the use of this couple. Later, before a steady state was reached, other couples were apparently affected by stray currents from the power circuits, which impressed E.M.F.'s of a few millivolts across some of the thermocouples. The E.M.F. of the couples would not remain constant, but varied with variations in the power circuit. If readings were taken while the power was off, the couples remained steady and gave consistent results. Additional difficulties arose when three of the base metal couples, 6, 8, and 9,

became oxidized and began to give very uncertain readings, even when the power was turned off. The readings of these couples were disregarded entirely.

After sixteen days a steady state, (*O*), was reached, with the first couple at 1038° C. Readings were taken with the power momentarily shut off. The rate of cooling was so slow that no perceptible error was introduced by this procedure.

An atmosphere of oxygen, replenished daily, was maintained throughout all of the runs.

After this steady state (*O*) had been obtained, the apparatus was torn down. The Sil-O-Cel adjacent to the steel shell was quite moist, and was sufficiently conductive to cause considerable annoyance, because the thermocouple wires were protected only by asbestos tubing, where they passed through the Sil-O-Cel. As the insulation had been heated, the moisture of the interior region of the powder had been driven out and condensed next to the cool shell. The oxygen which had been swept through the apparatus each day had not been sufficient to evaporate the water.

The Sil-O-Cel was removed while the cylinder was still hot and the stray currents in all of the couples disappeared. This difficulty with stray currents could have been avoided by having moisture proof insulation for the couples where they passed through the Sil-O-Cel.

All of the oxide which had been heated above 750° C. was thoroughly sintered. The Usalite protection tubes were so brittle after their long heating that they invariably broke when the oxide was chiseled away. The Alumel wires of the base metal couples were so thoroughly oxidized that they fell apart at the least disturbance. This was the cause of the failure of couples 6, 8, and 9. Couples 1, 2, 3, 5, 7, 11, and 12 were carefully re-calibrated as before, with the results shown in Table III.

The Platinum-Rhodium wires of the noble metal couples were covered with a thin layer of a black substance, possibly some oxide. The Usalite protection tubes of the inner couples were colored a deep brown, the depth of color becoming less as the radial distance increased, and was entirely absent on tubes that had not been heated above 900° C. It was probably caused by reaction with the iron oxide.

A representative sample was taken of the oxide in the cylinder, and analyzed for ferrous iron. Six determinations showed 0.00 per cent ferrous iron.

TABLE III

RESULTS OF RECALIBRATION OF THERMOCOUPLES (BY COMPARISON OF NEW CURVE WITH ORIGINAL CALIBRATION CURVE)

Couple.	Max. Temp. to Which the Couple Had Been Heated.	Degrees of Error at Designated Temperatures °C.					
		400	500	600	700	800	900
Noble metal							
1.....	1039	- 19	- 24	- 26	- 28	- 30	- 32
2.....	980	- 7	- 10	- 13	- 15	- 17	- 20
3.....	938	- 6	- 8	- 10	- 11	- 14	- 15
5.....	911	- 2	- 4	- 5	- 6	- 7	- 8
Base metal							
7.....	817	+ 16	+ 17	+ 18	+ 20	+ 21	
11.....	688	+ 5	+ 6	+ 7	+ 11	+ 12	
12.....	668	+ 1	0	+ 1	+ 2	0	

It is very evident that the errors are due to contamination and are dependent upon the maximum temperature to which the couple had been exposed.

In the last steady state, the temperature of couple number 5 was 911° C., and that of number 12 was 668° C. It is very probable, then, that the noble metal couples were not in error until they had been maintained at a temperature above 800° for a considerable length of time, while the base metal couples were free from error until after they had been heated above 650° C. Accordingly no correction need be applied until after steady state *N*.

These data are plotted in Fig. 8.

Careful study of the data plotted in Fig. 8 reveals that several couples consistently lie above or below the most probable smooth curve which might be drawn through the points. These apparent errors are probably errors in the effective position of the hot junction of the couple, because the effective position of the bead may easily vary more than one millimeter from position of the bead as computed from measurements of the outside of the protection tube. Errors of this kind should be constant throughout the work, and should be subject to correction. These corrections were made by computing the most probable curve representing the data of the equilibrium states *M* and *N*. This was done by the method of least squares,⁴⁴ assuming the data to be best represented by the equation

$$T = a + b \log r + c (\log r)^2$$

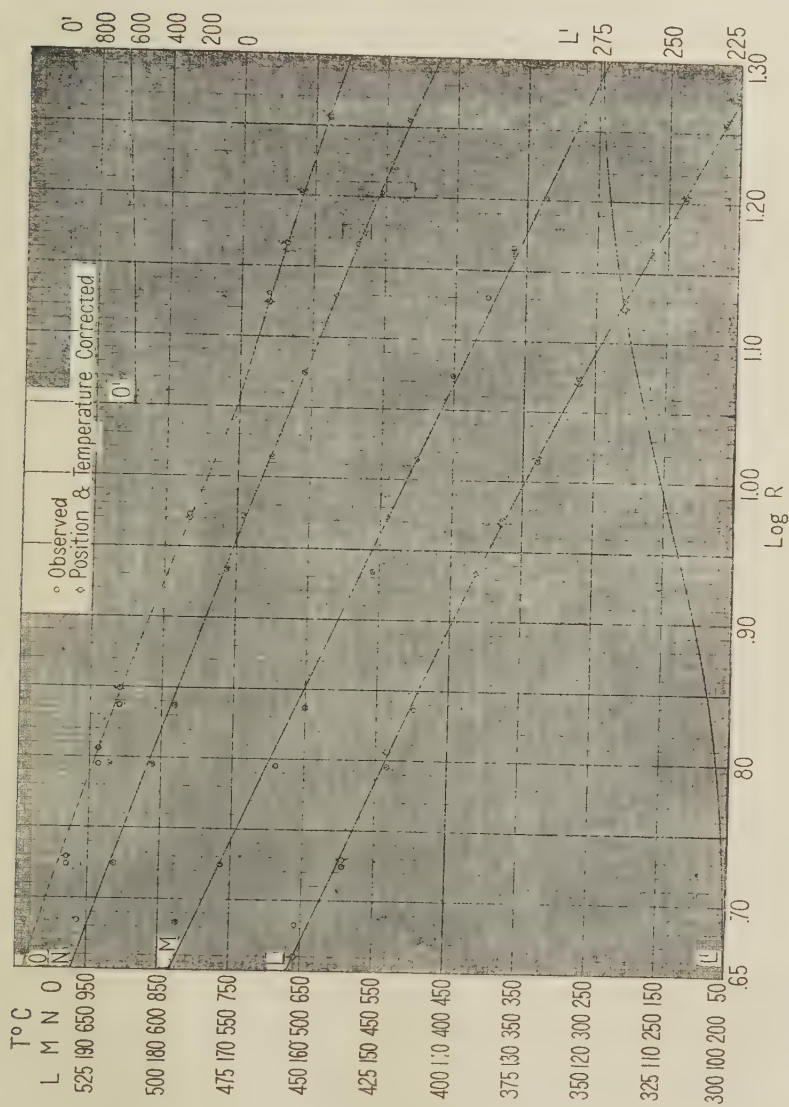


FIG. 8. Steady States

TABLE IV
DATA TAKEN DURING STEADY STATES

Couple	Temperature, °C. During Steady State.					Measured Radius, cm.	log ₁₀ <i>r</i>	log ₁₀ <i>r</i> Corrected.
	<i>L</i>	<i>M</i>	<i>N</i>	<i>O</i> Uncor- rected.	<i>O</i> Cor- rected.			
1....	452	177.5	657	1005	1039	4.83	.6840	.660
2....	436	171.5	632	959	980	5.30	.7243	.727
3....	421	164	606	923	938	6.24	.7952	.802
5....	412	160	591	903	911	6.87	.8370	.844
6....	391	151	557			8.59	.9340	.936
7....	382	149	546	838	817	9.38	.9722	.971
8....	370	145	527			10.34	1.0145	1.0163
9....	356	140	505			11.87	1.0745	1.072
10....	340	135.5	484	726	712(?)	13.50	1.1303	1.126
11....	330	132	469	699	688	14.66	1.1661	1.164
12....	319	127.5	453	668	668	15.92	1.2019	1.203
14....	305	122	434	630	630	18.00	1.2553	1.257

Watts

Power.	224	74.4	386	703			
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because the data are closely represented by the equation

$$T = a + b \log r.$$

The curves drawn through the data points of the steady states *M* and *N* in Fig. 8 represent the most probable values of temperature as computed by the method of least squares.

The data of steady state *O* could not be used in this way because there are at least two, and possibly three, transition points in the range of temperature involved.

Time-temperature curves show (Figs. 1 and 2), that there is another transition point at 360° C. For this reason the cylinder was not homogeneous at steady state *L*, and a continuous curve cannot represent the data.

The positions of the couples not on the curve were corrected by changing the abscissa of the point the required amount to make it fall on the curve. These positions were then averaged and used to aid in drawing the most probable curve through the data points of steady states *L* and *O*.

Tentative corrected values for the position of the thermocouples were computed by averaging the corrected values as obtained from the least square curves of steady states *M* and *N*, and from the smooth curve drawn through the plotted data of steady state *L*. These corrected values of $\log_{10} r$ are given in the last column of Table IV.

As the precision of temperature measurement is not greater than $\pm 1^\circ \text{C.}$, and all data points have a temperature (ordinate) error of less than 1°C. , after the correction for position has been applied, the steady state data are consistent within the experimental error.

The curves for $T \log_{10} r$ from the steady states *L* and *O*, were differentiated graphically, giving the derived curves *L'* and *O'* in Fig. 8. The corresponding curves for steady states *M* and *N* were formally differentiated by means of the least square equations.

In order to use these derivatives in equation (16) the rate of heat supply must be accurately determined in calories per second per unit of length of cylinder.

By definition

$$K = - \frac{\frac{\partial Q}{\partial t}}{\frac{2\pi}{2.303} \frac{\partial T}{\partial \log r}}. \quad (16)$$

Since the energy input is measured in watts in a heating element 76.3 cm. long, the equation becomes.

$$K = - \frac{\text{Power in Watts}}{\frac{4.19 \times 2\pi \times 76.3}{2.303} \frac{\partial T}{\partial \log r}}$$

or

$$K = - \frac{\text{Power in Watts}}{873.3 \frac{\partial T}{\partial \log r}}. \quad (16a)$$

The power measurements of the steady states were the cause of some difficulty. The voltage leads were made of Chromel A wire fastened directly to the top of the heating element. The only method of fastening which could be used was to twist the wires. Brass connectors were out of the question, and welded wires are very apt to be brittle. After the first two steady states, the wires had evidently oxidized sufficiently to make a poor contact. The

voltage readings began to fall off, indicating an apparent lowering of resistance in the heating element as the temperature increased. This is contrary to the known properties of the wire, and is evidence of a corresponding error in the power readings. It was therefore necessary to calculate the resistance indirectly.

The temperature coefficient of resistance of Chromel A wire is quite small, according to the Hoskins Company it is 0.00011 per 1° C.

$$R = R_0(1 + 0.00011T),$$

where R is resistance at T° C., and R_0 is resistance at 0° C. In order to compute R_0 it was necessary to determine R at some known temperature. The length of wire in the heating element was 1224 cm. The resistance of the wire had been previously determined, by means of a Wheatstone bridge, to be 0.158 ohms per foot, or 0.005184 ohms per cm., at 20° C. The resistance of the heating element, as computed from the above measurements, was 6.344 ohms at 20° C.

$$R_0 = 6.33 \text{ ohms.}$$

In order to calculate the resistance for a steady state, it was necessary to assume a temperature for the wire. This, of course, was a source of error, but since the temperature coefficient is so small, it is probably less than 2 per cent. The results of the computation are listed in the following table.

TABLE V
RESISTANCE OF HEATING ELEMENT

Steady State.	I	E	Temp. in $^{\circ}$ C. Couple No. 1.	Assumed Wire Temp.	Measured R (Ohms).	Calculated R (Ohms).
<i>L</i>	5.77	38.81	452.0	650	6.74	6.78
<i>M</i>	3.36	22.17	177.5	350	6.60	6.58
<i>N</i>	7.43	48.50	657.0	900	6.52	6.98
<i>O</i>	9.88	65.54	1039.0	1250	6.64	7.21

Only in steady states *N* and *O* is it necessary to use the calibrated values of resistance. The values of $(\partial T / \partial \log_{10} r)$ can now be substituted in equation (16a), giving the results tabulated in Table VI.

TABLE VI
THERMAL CONDUCTIVITY OF POWDERED Fe_2O_3

Temperature °C.	Cal./sec./cm. ² /cm./°C.	Steady State.	Method of Evaluation of Derivative.
125.....	0.000918	<i>M</i>	Least Squares
150.....	0.000925	<i>M</i>	Least Squares
175.....	0.000930	<i>M</i>	Least Squares
300.....	0.000940	<i>L</i>	Graph. Differ.
350.....	0.000980	<i>L</i>	Graph. Differ.
400.....	0.00108	<i>L</i>	Graph. Differ.
450.....	0.00113	<i>L</i>	Graph. Differ.
450.....	0.00109	<i>N</i>	Least Squares
500.....	0.00113	<i>N</i>	Least Squares
550.....	0.00117	<i>N</i>	Least Squares
600.....	0.00122	<i>N</i>	Least Squares
650.....	0.00127	<i>N</i>	Least Squares
650.....	0.00128	<i>O</i>	Graph. Differ.
700.....	0.00133	<i>O</i>	Graph. Differ.
750.....	0.00138	<i>O</i>	Graph. Differ.

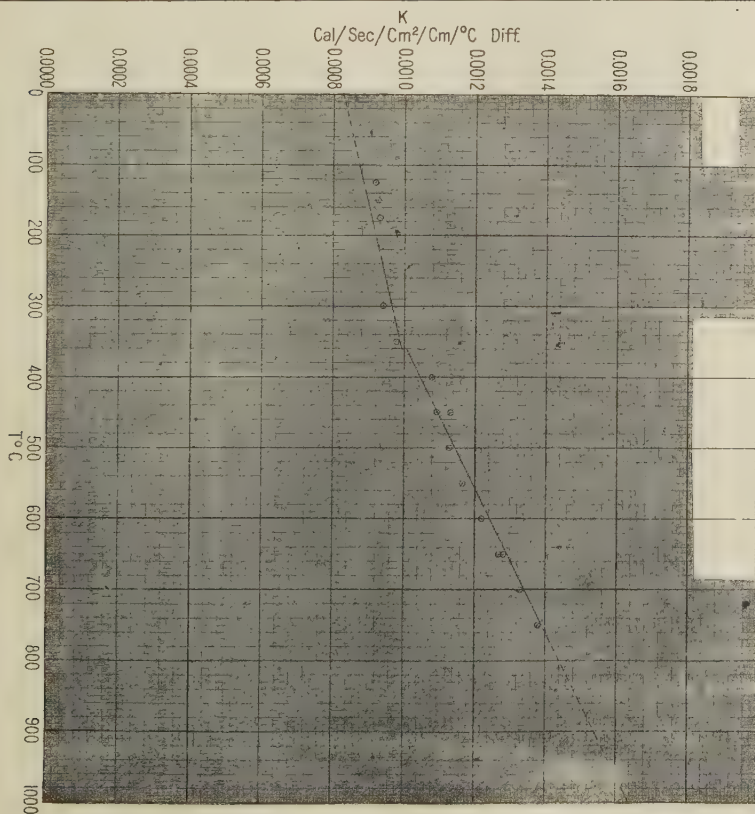


FIG. 9. Thermal Conductivity of Powdered Ferric Oxide

The data of Table VI have been checked by calculations using the integrated form of the equation given as equation 7, and are plotted in Fig. 9. As an error in the measurement of the power consumed during a steady state introduces a similar direct error in the numerical value of K (see equation (16a)), and the rate of change of K with temperature (dK/dT) seems to be approximately constant, any errors in power measurement cause an error in the values of K but not in (dK/dT) for a given steady state. Accordingly the data are best interpreted by drawing a straight line through the computed

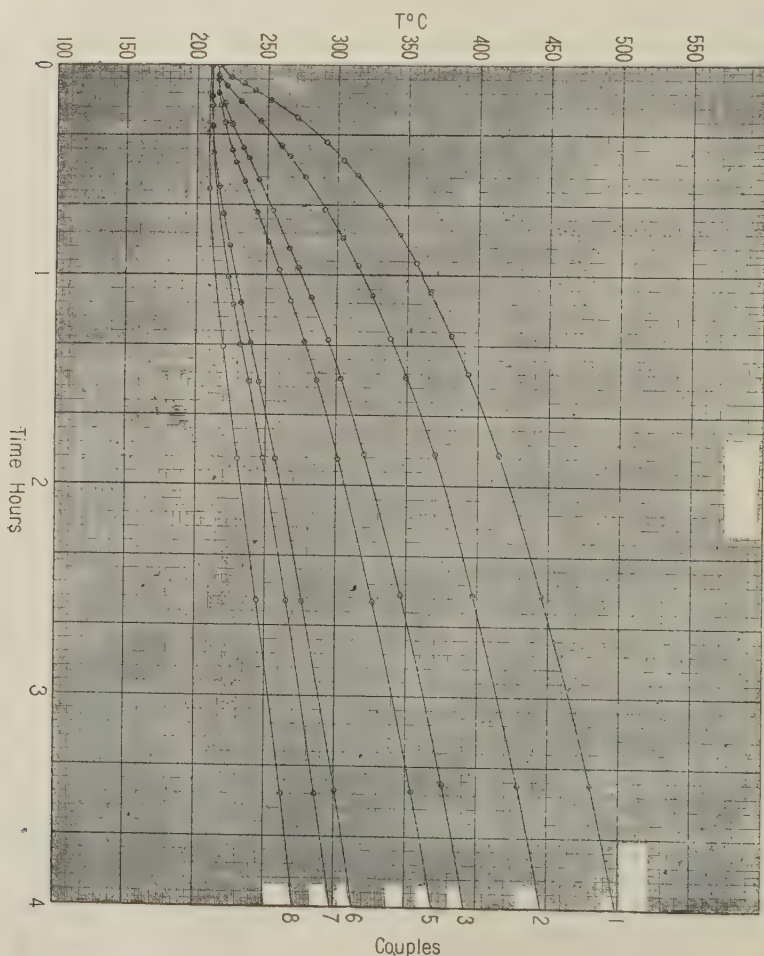


FIG. 10. Run 2

values, the slope of which is the average of the slopes of the various lines which might be drawn through the different groups of data.

The variation of the conductivity with temperature is interpreted as a straight line function because the inaccuracies of the data do not justify the use of a curve of higher degree.

The transition point at 360° C. causes a decided break in the conductivity curve. The conductivity was not evaluated above 750° C. because the temperature data were not sufficiently accurate to justify the computation of specific heats beyond that point.

CALCULATION OF SPECIFIC HEAT

The time-temperature data of each thermocouple, taken during the runs (2, 3, and 4), between the steady states, are plotted in Figs. 10, 11, 12, and 13.

Equation (14),

$$CD \frac{\partial T}{\partial t} = \frac{1}{2.303^2} \left[\frac{K}{r^2} \frac{\partial^2 T}{\partial \log_{10} r^2} + \frac{1}{r^2} \frac{dK}{dT} \left(\frac{\partial T}{\partial \log_{10} r} \right)^2 \right],$$

offers advantages over equation (13) in containing one less term, and $(\partial T / \partial \log_{10} r)$ is more easily and accurately obtainable than $\partial T / \partial r$ because the latter is large and changes very rapidly with r .

The temperature-time curves for run 2, Fig. 10, were differentiated graphically over the first two hours, giving the first derived curves $\partial T / \partial t$ plotted in Fig. 14.

The temperatures of a number of couples at the same time were plotted against $\log r$. This curve, T in Fig. 15, was graphically differentiated, giving the first derived curve T' , which in turn was differentiated, giving the second derived curve T'' . All the quantities necessary for the solution of equation (14) for specific heat, C , were then available. D was taken as constant and equal to 2.79, as determined.

The second derivative, $(\partial^2 T / \partial \log_{10} r^2)$, is so sensitive to small changes in the integral curves that a slight change in the choice of the curve through the data points makes a large difference in the computation. There are always several slightly different, equally justifiable curves which may be drawn through observed data points.

In these calculations it is possible to compute the specific heat at a given temperature from a great number of data obtained at different times, and at different parts of the cylinder. As the

material is homogeneous, the results computed from these different data must be consistent. Because of this fact, the method makes

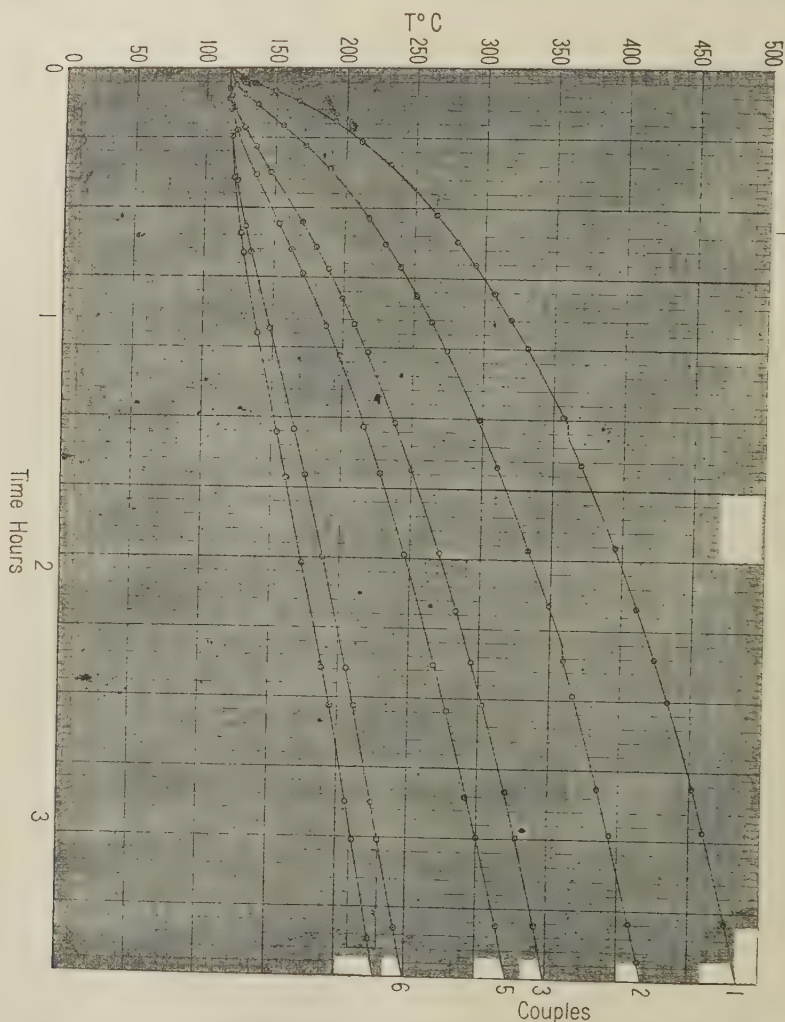


FIG. 11. Run 3

possible a great number of check solutions for each temperature, and provides additional knowledge as to the correct way in which the integral curve should be drawn. A further aid is the fact that

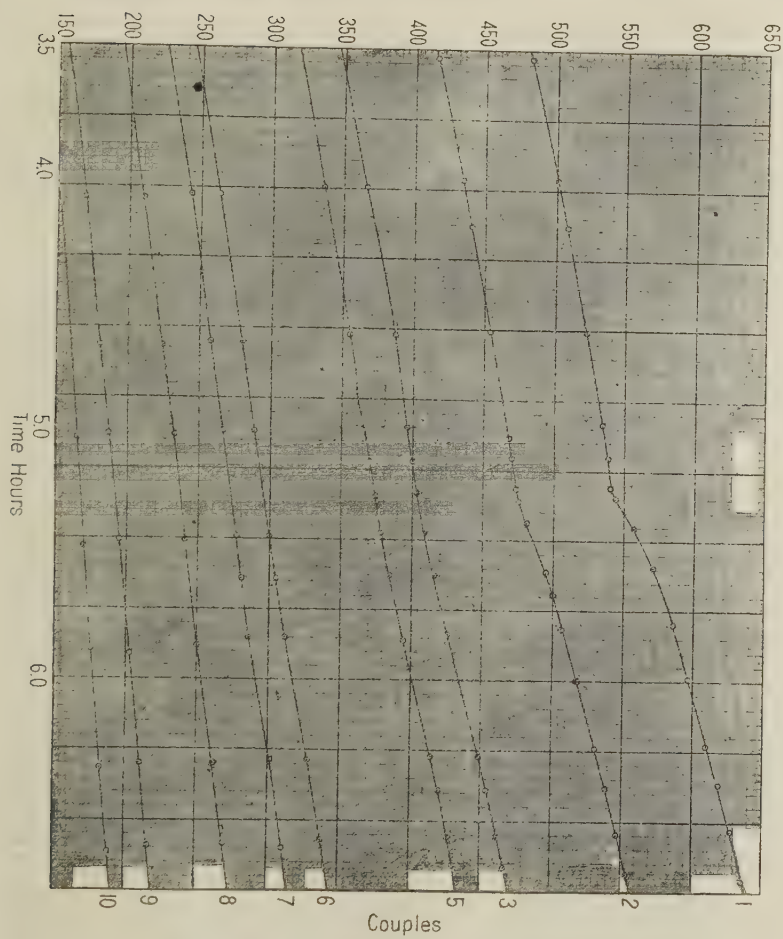


FIG. 12. Run 3

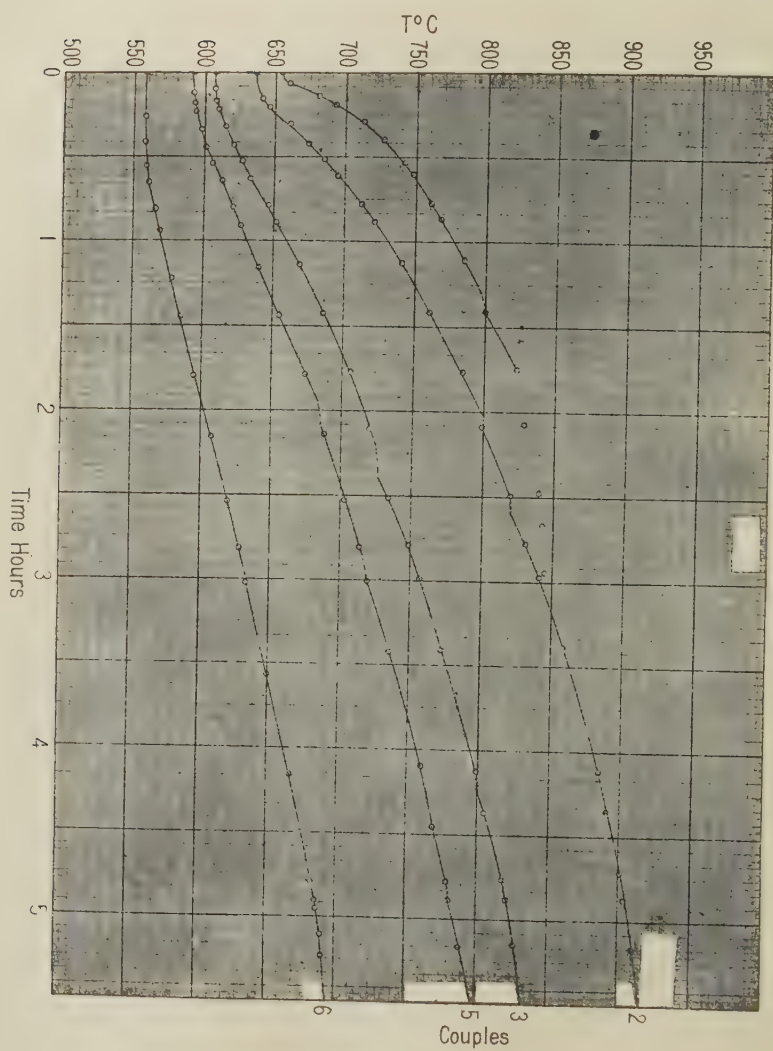


FIG. 13. Run 4

all known specific heat data are increasing continuous functions of temperature, except when passing through a transition point or range.

This correct curve must give results consistent with themselves, and with other results similarly computed from other data of the same kind in the same cylinder. This process of selecting curves

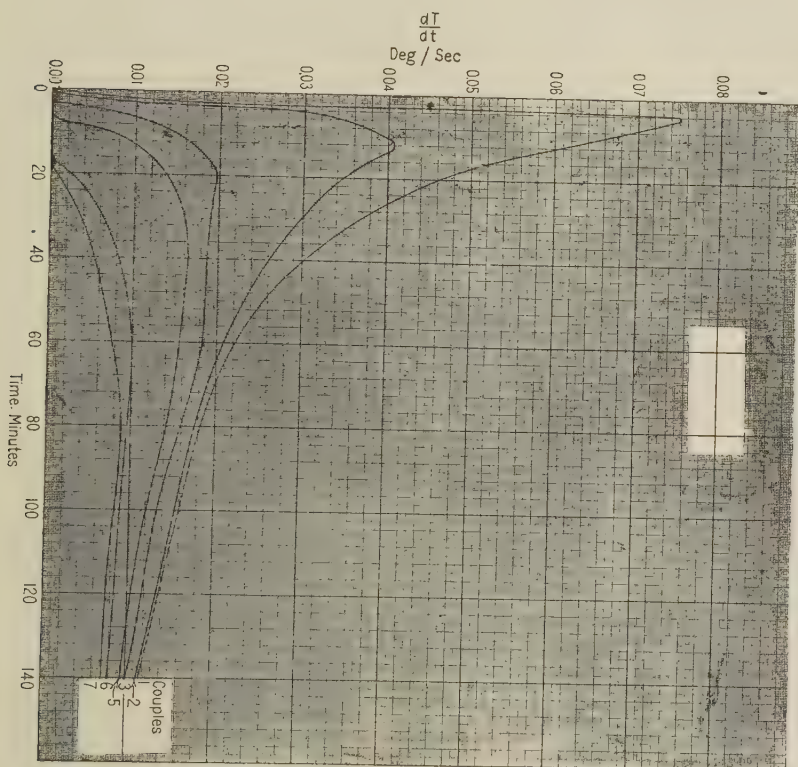


FIG. 14. Run 2

must not be confused with a process of rationalizing data. By use of this additional information it is possible to select the integral curve which gives consistent results and designate it the correct one.

It is permissible to apply small additional corrections to the couple positions, if the corrections are used consistently, for an element of uncertainty exists concerning the exact effective position,

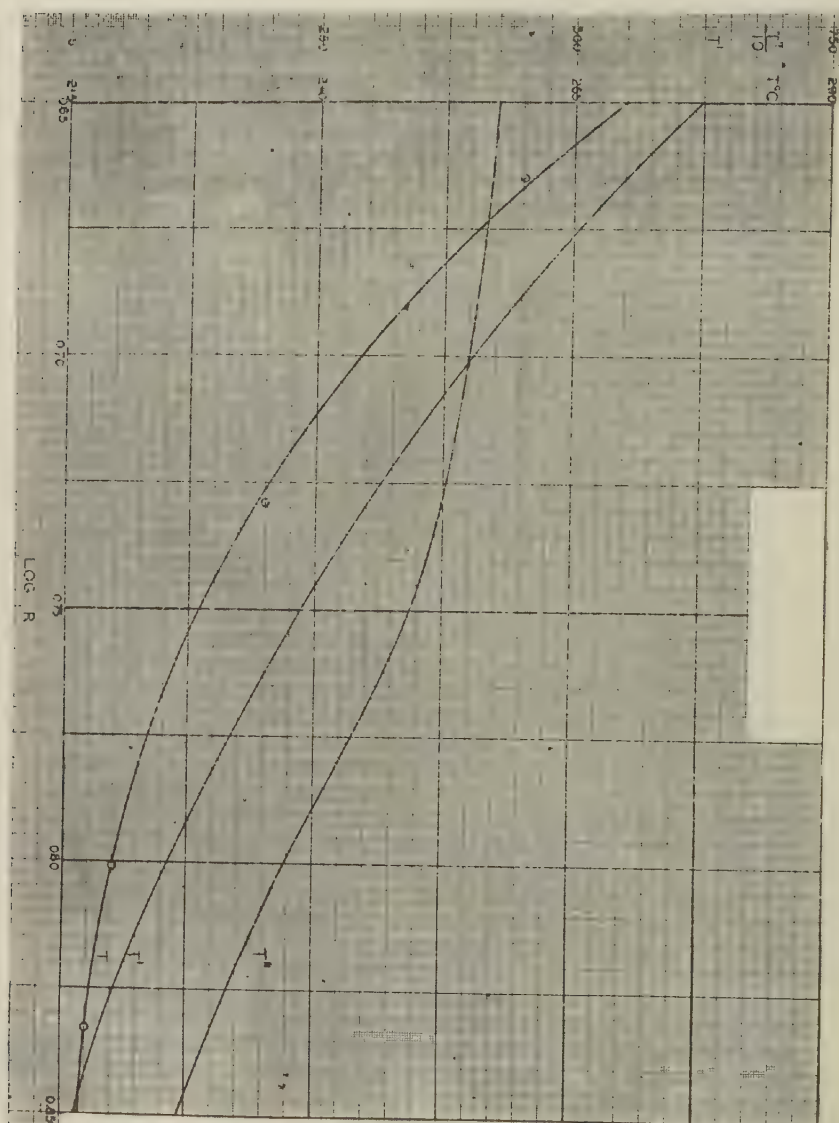


FIG. 15. Run 2 at 12 Min.

even after the corrections computed for the steady states are applied. As the temperature data are accurate only to 2° C., a point may be removed from the curve by as much as 2° C., if so demanded by check computations from other data.

The many check computations are tedious but workable. The work may be considerably shortened by taking the T -log r curves in sections of 4, 5, or 6 points each, as a small number of points limits the number of possible curves. The rate of temperature rise for the six outside couples was so small that their data were not satisfactory for specific heat computations, and were for this reason generally omitted.

TABLE VII
CORRECTED COUPLE POSITIONS

Couple.	Corrected.		Measured r (cm.)	Couple.	Corrected.		Measured r (cm.)
	log r	r (cm.)			log r	r (cm.)	
1.....	0.665	4.62	4.83	8.....	1.016	10.38	10.34
2.....	0.729	5.36	5.30	9.....	1.072	11.80	11.87
3.....	0.801	6.32	6.24	10.....	1.127	13.40	13.50
5.....	0.833	6.81	6.87	11.....	1.164	14.59	14.66
6.....	0.937	8.65	8.59	12.....	1.203	15.96	15.92
7.....	0.971	9.35	9.38	14.....	1.257	18.07	18.00

SAMPLE COMPUTATION FOR SPECIFIC HEAT AT 260° C., AND RADIAL DISTANCE
4.62 CENTIMETERS

Data for Run 2, Time 12 Minutes

Figure.	Quantity.	Couple.			
		1	2	3	5
10.....	T° C.	260	235	220	217.5
15.....	$\frac{\partial T}{\partial \log r}$	- 550	- 325	- 105	- 25
15.....	$\frac{\partial^2 T}{\partial \log r^2}$	4200	3750	2200	1450
15.....	log r	0.665	0.729	0.801	0.833
15.....	r	4.62	5.36	6.32	6.81
14.....	$\frac{\partial T}{\partial t}$	0.0605	0.0407	0.0166	0.0095
9.....	K	0.00095	0.00094	0.00092	0.00092
9.....	$\frac{dK}{dT}$	0.0000005	0.0000005	0.0000005	0.0000005

Some of the couple positions were further corrected by means of the large number of check solutions available from specific heat computations. The radial distances, after these final corrections, are given in Table VII.

$$CD \frac{\partial T}{\partial t} = \frac{1}{2.3^2} \left[\frac{K}{r^2} \frac{\partial^2 T}{\partial \log_{10} r^2} + \frac{1}{r^2} \frac{dK}{dT} \left(\frac{\partial T}{\partial \log_{10} r} \right)^2 \right]. \quad (14)$$

At couple number 1

$$r^2 = 21.3, \quad \left(\frac{\partial T}{\partial \log r} \right)^2 = 302,500,$$

$$D = 2.79, \quad (2.303)^2 = 5.30,$$

$$2.79 \times 0.0605 C = \frac{1}{5.3} \left[\frac{0.00095 \times 4200}{21.3} + \frac{302500 \times 0.00000065}{21.3} \right]$$

$$= \frac{0.187 + 0.0071}{5.3} = 0.0367,$$

$$C = 0.217.$$

RESULTS OF SPECIFIC HEAT COMPUTATIONS

Run 2, 12 minutes

Couple.	$T^\circ \text{C.}$	$\frac{\partial T}{\partial \log r}$	$\frac{\partial^2 T}{\partial \log r^2}$	$\frac{\partial T}{\partial t}$	K	$\frac{dK}{dT}$	C
1.....	260.0	— 550	4200	0.0605	0.00095	0.5×10^{-6}	0.217
2.....	235.0	— 325	3750	0.0407	0.00094	0.5×10^{-6}	0.207
3.....	220.0	— 105	2200	0.0166	0.00092	0.5×10^{-6}	0.207
5.....	217.5	— 25	1450	0.0095	0.00092	0.5×10^{-6}	0.204

Run 3, 10 minutes

1.....	177.5	— 780	6150	0.0950	0.00091	0.5×10^{-6}	0.197
2.....	141.0	— 400	5250	0.0600	0.00089	0.5×10^{-6}	0.186
3.....	120.5	— 140	2600	0.0210	0.00088	0.5×10^{-6}	0.184
5.....	118.0	— 65	170	0.0120	0.00088	0.5×10^{-6}	0.182

Run 3, 1 hour

1.....	319.5	— 975	1745	0.0308	0.00097	0.5×10^{-6}	0.223
2.....	262.0	— 850	2175	0.0256	0.00095	0.5×10^{-6}	0.222
3.....	206.5	— 637	3180	0.0248	0.00094	0.5×10^{-6}	0.217
5.....	190.5	— 540	3560	0.0235	0.00092	0.5×10^{-6}	0.211
6.....	146.2	— 195	3000	0.0131	0.00089	0.5×10^{-6}	0.187

Run 3, 1 hour, 20 minutes

1.....	353.5	— 1010	1500	0.0265	0.00099	0.5×10^{-6}	0.238
2.....	294.0	— 900	1950	0.0245	0.00097	0.5×10^{-6}	0.220
3.....	232.5	— 750	2400	0.0199	0.00093	0.5×10^{-6}	0.214
5.....	210.7	— 680	2600	0.0185	0.00092	0.5×10^{-6}	0.206
6.....	162.0	— 280	2950	0.0129	0.00090	0.5×10^{-6}	0.189

Run 3, 5 hours, 30 minutes

1.....	567.0	— 1200	800	0.0245	0.00123	10 ⁻⁶	0.314
2.....	490.0	— 1150	1000	0.0202	0.00115	10 ⁻⁶	0.288
3.....	412.5	— 1080	850	0.0130	0.00109	10 ⁻⁶	0.273
5.....	381.5	— 1050	875	0.0114	0.00104	10 ⁻⁶	0.264

Run 3, 6 hours, 10 minutes

1.....	607.0	— 1200	0	0.0136	0.00128	10 ⁻⁶	0.335
2.....	526.0	— 1193	200	0.0134	0.00116	10 ⁻⁶	0.291
3.....	442.5	— 1155	825	0.0132	0.00110	10 ⁻⁶	0.287
5.....	409.5	— 1125	1012	0.0126	0.00107	10 ⁻⁶	0.272

Run 3, 6 hours, 40 minutes

1.....	631.0	— 1230	0	0.0140	0.00130	10 ⁻⁶	0.342
2.....	550.0	— 1230	0	0.0120	0.00118	10 ⁻⁶	0.298
3.....	464.5	— 1220	337	0.0116	0.00113	10 ⁻⁶	0.271
5.....	428.5	— 1210	414	0.0105	0.00109	10 ⁻⁶	0.270

Run 4, 20 minutes

1.....	718.5	— 950	3100	0.0433	0.00136	10 ⁻⁶	0.376
2.....	663.0	— 760	3100	0.0333	0.00131	10 ⁻⁶	0.328
3.....	616.0	— 580	2000	0.0150	0.00126	10 ⁻⁶	0.322
5.....	597.5	— 520	1550	0.0100	0.00124	10 ⁻⁶	0.320

Run 4, 1 hour, 40 minutes

2.....	778.0	— 1118	1275	0.0190	0.00142	10 ⁻⁶	0.380
3.....	700.0	— 1013	1910	0.0165	0.00134	10 ⁻⁶	0.367
5.....	668.0	— 946	2320	0.0160	0.00131	10 ⁻⁶	0.358
6.....	591.0	— 600	2620	0.0100	0.00124	10 ⁻⁶	0.326

The results of the specific heat computations are plotted in Fig. 16. Table VIII gives the values of specific heat as read from the curve from 0° to 650° C.

TABLE VIII
SPECIFIC HEAT OF FERRIC OXIDE, (Fe₂O₃)

Temp. °C.	Heat Capacity cals. per gram.	Temp. °C.	Heat Capacity cals. per gram.
0.....	.150	260.....	.216
20.....	.158	280.....	.2205
40.....	.164	300.....	.225
60.....	.1695	320.....	.2295
80.....	.175	340.....	.234
100.....	.180	360.....	.2385
120.....	.1845	380.....	.2525
140.....	.189	400.....	.2645
160.....	.1935	450.....	.280
180.....	.198	500.....	.2955
200.....	.2025	550.....	.311
220.....	.207	600.....	.326
240.....	.2115	650.....	.342

The values of specific heats above 650°C. are those of a superheated oxide because transitions begin in the neighborhood of 675°C. and continue up to about 800°C. Three transitions have been

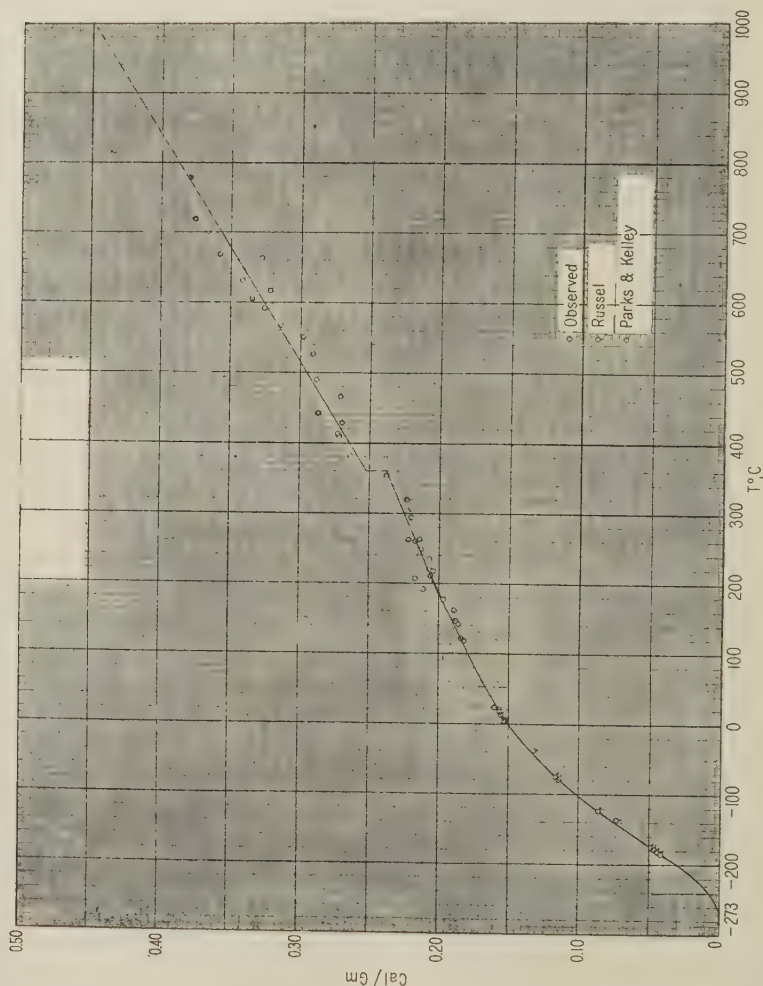


FIG. 16. Specific Heat of Ferric Oxide

found in this region by other investigators. The curves of Fig. 13 show a number of decided breaks which are undoubtedly due to transitions, but these changes are scattered throughout the tem-

perature range, showing that the temperature of transition depends upon the rate of heating, as it shows a considerable lag in the region of the inside couples where the heating is rapid. The data above the transition range were unreliable because the couples were then in error, due to contamination, and accurate readings were impossible, due to stray e.m.f.'s.

The best straight lines are drawn through the plotted computed values above 360° C. in Fig. 16. The data given in Fig. 16 all agree within ± 5 per cent.

ALLOTROPIC TRANSFORMATIONS

Table IX is believed to be a complete summary of the available information of the allotropic transformations in the common iron oxides.

TABLE IX
TRANSITION POINTS OF IRON OXIDES

Substance.	Temperature of Transition, $^{\circ}$ C.	Energy Change.	Reference.
Fe_2O_3	678	No data	Sosman and Hostetter ⁴⁵
Fe_2O_3	755-785	No data	Sosman and Hostetter
Fe_2O_3	720	No data	Bidwell ⁴⁶
Fe_2O_3	1320	No data	Bidwell
Fe_2O_3	1035	No data	Kohlmeyer ⁴⁷
Fe_2O_3	1250-1350	No data	Kohlmeyer
Fe_3O_4	525	No data	Wologdine ⁴⁸
Fe_3O_4	530	No data	Sosman ⁴⁹
Fe_3O_4	535	No data	Curie ⁵⁰
Fe_3O_4	580	14.4 cal./gm. (calc.)	Weiss and Beck ⁵¹
Fe_3O_4	581	No data	Weiss and Foe ⁵²
Fe_3O_4	570	No data	Chaudron and Forestier ⁵³
Fe_3O_4	500	No data	Chaudron and Forestier
FeO	No data		

NEW TRANSITION POINT AT 360° C. AND HEAT OF TRANSITION

Figure 11 shows that the iron oxide between couples 1 and 2 absorbed heat at a temperature of not less than 359° C. or more than 360° C. without a corresponding increase in temperature during the time interval from 1 hour 20 minutes to 2 hours 25 minutes. This absorption of heat at constant temperature can be accounted for only by the existence of an allotropic transformation at 359° - 360° C

The existence of such a transition point at this temperature was checked by means of a Leeds and Northrup differential thermocouple transformation point recorder. This machine is designed for use with metals and will not give sharp peaks in the heating or cooling

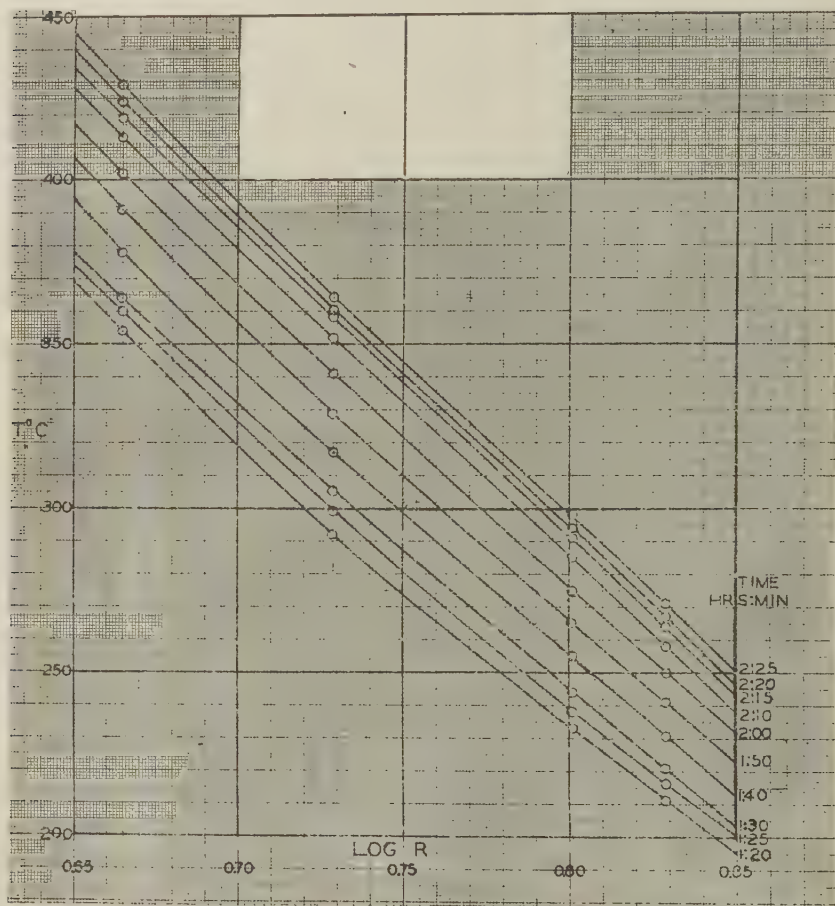


FIG. 17. Run 3 at First Transition

curves of powdered materials. But decided deflections were observed when heating or cooling a sample of the oxide between 300° C. and 400° C. The heating curve showed a deflection indicating absorption of heat beginning at 370° C. and continuing to 395° C. The cooling curve showed a deflection indicating evolution of heat.

beginning at 350°C. and continuing to 320°C. Slower heating and cooling of another sample showed deflections from 365° to 385°C. and 352° to 335°C. Making allowance for the lag in these deflec-

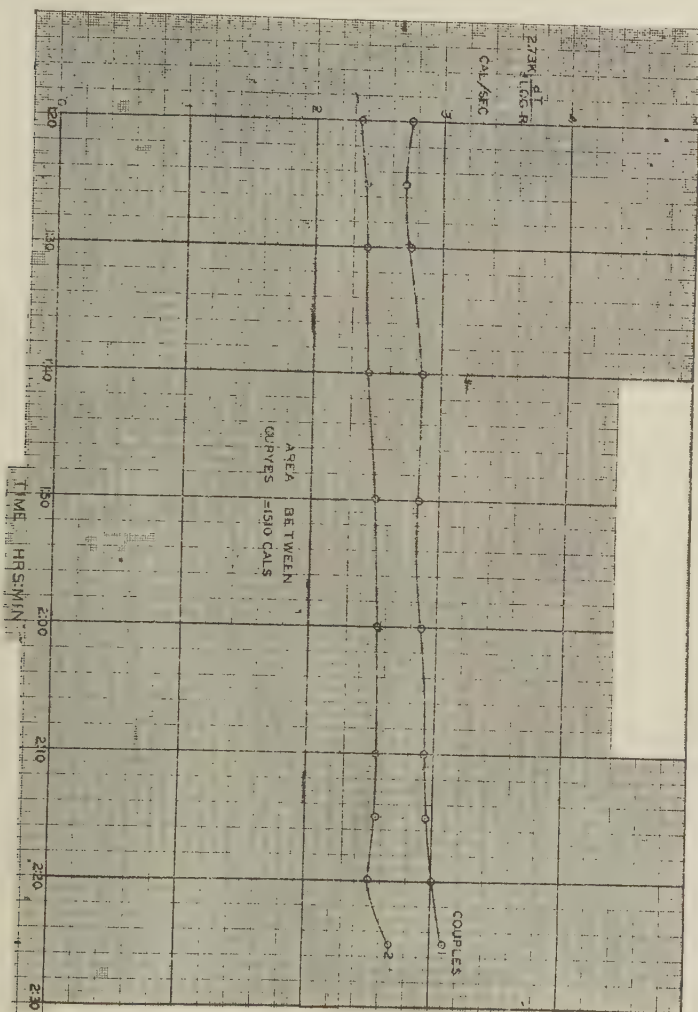


FIG. 18. Run 3, First Transition

tions the temperature of transition is found to be about 360°C. or slightly less. This is an excellent check with the results indicated by Fig. 9.

The heat of transition is determined by subtracting from the total heat absorbed computed by using equation 18 as described in Part I, the sensible heat absorbed computed by using equation 19 as above. As the transformation was completed between couples 1 and 2 in the time interval between 1 hour 20 minutes and 2 hours 25 minutes the $T - \log_{10} r$ curves (at constant time t) are plotted in Fig. 17 for 10 different times during this interval. Each of these curves was differentiated at couple number 1 and couple number 2, to evaluate $-(\partial T / \partial \log_e r)$ for substitution in equation (17),

$$\frac{\partial Q}{\partial t} = K2\pi \left(- \frac{\partial T}{\partial \log_e r} \right).$$

Equation (17) may be written

$$\frac{\partial Q}{\partial t} = - \frac{2\pi}{2.303} K \frac{\partial T}{\partial \log_{10} r} = - 2.73 K \frac{\partial T}{\partial \log r}. \quad (17a)$$

The values of the right hand member of equation (17a), for both couple 1 and couple 2, are plotted in Fig. 18. The area between these curves is equal to the total accumulation of heat between r_1 and r_2 as given by equation (18).

Total heat absorbed

$$\Delta Q = \int_{t_1}^{t_2} - K2\pi \left(\frac{\partial T}{\partial \log_e r} \right)_{r_1} dt - \int_{t_1}^{t_2} - K2\pi \left(\frac{\partial T}{\partial \log_e r} \right)_{r_2} dt. \quad (18)$$

This area in Fig. 18 is equivalent to 1,510 calories.

The Sensible heat absorbed is given by equation (19).

$$\text{Sensible Heat absorbed} = 2\pi D \int_{r_1}^{r_2} r dr \int_{T_1}^{T_2} c dT. \quad (19)$$

Each integration must be done graphically. The variation of specific heat with temperature is taken as a straight line function over narrow ranges given by the equation

$$C = 0.142 + 0.000306 T$$

and below 360°C. by the equation

$$C = 0.161 + 0.000214 T.$$

Above $360^\circ \text{C.},$

$$\int_{360}^{T_2} C_p dT = \int_{360}^{T_2} 0.142 dT + \int_{360}^{T_2} 0.000306 T dT.$$

Below 360°C. ,

$$\int_{T_2}^{360} C_p dT = \int_{T_2}^{360} 0.161 dT + \int_{T_2}^{360} 0.000214 T dT.$$

Substitution in equation (19),

Sensible heat absorbed

$$= 2\pi D \int_{r_1}^{r_2} r dr \left[\int_{T_1}^{360} C_p dT + \int_{360}^{T_2} C_p dT \right]. \quad (19a)$$

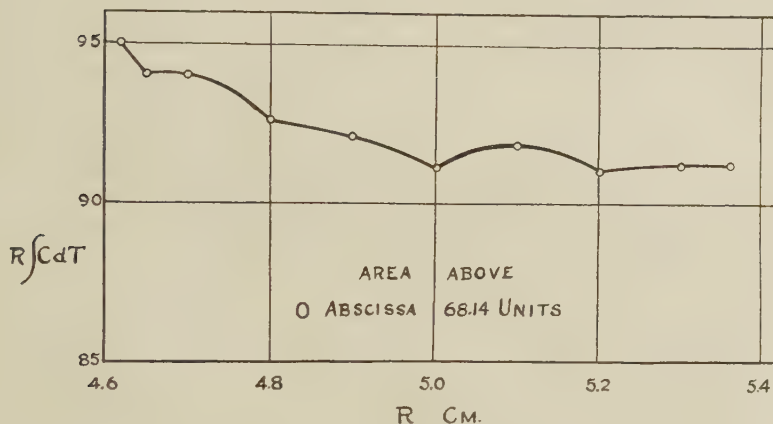


FIG. 19. Run 3, First Transition

Temperature limits T_1 and T_2 for various radial distances between r_1 and r_2 , for the entire time under consideration, are taken from the curves of Fig. 17 and substituted in equation (19a).

$r \left[\int_{T_1}^{360} C_d T + \int_{360}^{T_2} C_d T \right]$ is plotted against r , in Fig. 19.

The integrated value of the curve between r_1 and r_2 is 68.14 units. Multiplying this by $2\pi D$ gives

Sensible Heat absorbed $= 2\pi \times 2.79 \times 68.14 = 1,195$ calories.

The total heat absorbed, computed by equation (18), is 1510 calories. The difference, 315 calories, is the heat of transition.

The mass of material is

$$\pi D(r_1^2 - r_2^2) = \pi \times 2.79(5.36^2 - 4.62^2) = 65 \text{ grams.}$$

Therefore the heat of transition $= 315/65 = 4.85 \text{ cal./gm.}$

TRANSITIONS 650°–825° C.

The transformations between 650° and 825° C. have such a tendency to lag that it is not possible to handle them as separate entities without more complete data. For this reason the heats of the transitions in the temperature range 650° to 825° C. are grouped together as one. For want of better data, it is necessary to consider that the specific heat throughout this range followed the same function that it did below 650° C.

The method of evaluation is exactly the same as was used for the transformation at 360° C., and for this reason is not given in detail.

The initial data is taken from run 4 in the time interval from 15 minutes to 5 hours, between couples 2 and 3. The integration of the rates of heat flow show a total accumulation of 12,586 calories.

The sensible heat absorbed was found to be 8,485 calories.

$$\text{Heat of transitions} = 12,586 - 8,485 = 4,101 \text{ cal.}$$

$$\text{Mass of material} = 2.79 \pi (r_3^2 - r_2^2) = 98.2 \text{ grams.}$$

$$\text{Heat of transition} = \frac{4101}{98.2} = 41.8 \text{ cal./gm.}$$

The probable error in the value of heat of transformation at 360° C. is about 10 per cent. Because of the extrapolation of the specific heat curve in the last determination, the error for the heats of transition between 650° and 825° C. is probably greater.

SOURCES OF ERROR

1. *Impurities in Oxide*

Since the oxide is about 99 per cent pure, with SiO_2 and MnO or Mn_2O_3 as the principal impurities, and the specific heats of these oxides are very comparable to that of Fe_2O_3 , it is improbable that the error at any temperature would exceed 0.5 per cent.

2. *Evaporation of Moisture*

This source of error was practically eliminated as the moisture was always completely evaporated from the oxide before any data were taken.

3. *Distance Measurements*

This source of error was largely eliminated by using the most probable curves of the data, as computed by the method of least squares.

4. *Presence of Couples in the Oxide*

The thermocouples and protection tubes are equivalent to so much impurity, concentrated in one place.

Any particular couple whose temperature is under consideration will give the average temperature of the small body of oxide immediately surrounding it, provided the temperature lag of the protection tube is not greater than that of the oxide. This was tested by heating two couples in the calibration furnace, one in a protection tube, the other bare, and observing the temperatures of each. With a temperature rise of 0.06°C. per second, which is 0.9 times the maximum rate of temperature rise in the oxide cylinder, the temperatures indicated by the two couples were identical, showing that the error due to protection tube lag can be disregarded.

The protection tube closest to the center had a cross-sectional area equal to 0.4 per cent of that of an annular ring of its own thickness, concentric with the heating element. As the various couples were dispersed throughout the entire angular distance, this inside couple had about the same effect as 0.4 per cent of any other impurity. The equivalent amount of impurity introduced by the other couples was much less.

5. *Power*

The source of power was found to be constant to 0.5 per cent. As the specific heat (C) is almost proportional to the thermal conductivity (K), which is directly proportional to the power, an error of 0.5 per cent in the power would cause the same error in the computed specific heat.

In computing the resistance of the heating element for determining the power input at higher temperatures, because of the failure of the potential connections, an error is introduced. If the estimated temperature of the heating element were as much as 200°C. in error, an error of about 2 per cent is introduced in the computed power.

6. *Instruments*

The type K potentiometer used for taking all readings is accurate to ± 0.0005 millivolts. This is about 0.1 per cent of the smallest reading taken, and is negligible.

As the volt box had a resistance of 10,000 ohms, compared to a maximum of 7 ohms in the heating element, the power loss through the volt box could never exceed 0.07 per cent of the total.

7. Time Reading

A 1/5 second stop watch was used for timing all readings taken while the temperature was rising rapidly. The maximum error of 1 second is smaller than can be shown on any of the graphs, and is negligible.

8. Tamping of Oxide

In preliminary tests oxide was tamped with a density constant within 0.72 per cent. As the specific heat is proportional to the density, the maximum error due to this cause is less than 1.0 per cent.

9. Temperature Measurements

Barring contamination and overheating, an individually calibrated couple is as accurate as its calibration. As the various calibration data are consistent within 2° C., the temperature readings are accurate to $\pm 1^\circ \text{C}$.

10. Heat Capacity of Gases between Particles of Oxide

From the true density, apparent density, and heat capacity of the oxide, and heat capacity and density of the gases in the tamped powder, it can be shown that the error introduced by neglecting the latter is less than 0.03 per cent.

11. Convection Currents in the Cylinder of Oxide

If in any part of the cylinder the air were being displaced once each second by air at a temperature differing by 1° C., the error would not exceed 1.5 per cent. Such rapid circulation is practically impossible. Attempts to force oxygen through the apparatus rapidly enough to change the temperature of any of the couples while the cylinder was at a steady state gave entirely negative results.

Suggested Improvements

Although noble metal couples are usually reliable up to at least 1,250° C., the couples used in this work began to fail at 900° C., due to failure of the Usalite protection tubes to adequately protect the couples from contamination. This contamination was due either to the material of the tube itself or to iron introduced through the protection tubes. A better means of protecting the thermocouples is necessary than a single two hole Usalite tube.

If the outside of the cylinder of oxide were surrounded by a heating element, so that the external temperature could be con-

trolled, the temperature gradients throughout the material could be controlled, and adjusted to make the computations more easy and accurate.

Advantages and Disadvantages

In brief, this method for determining the thermal properties of solids offers the following advantages.

As the set-up is made in a gastight cylinder, it is possible to maintain an atmosphere which will prevent conversion of the material. This makes the method especially advantageous for solids which are ordinarily unstable at the temperature of investigation, for instance, ferrous oxide.

It should be possible to effect desired changes of composition within the set-up, for instance, the conversion of ferric oxide into ferrous oxide by the introduction of an atmosphere of steam and hydrogen into the hot oxide.

This method permits the simultaneous determinations of thermal conductivity, specific heat, temperatures of transition, and heats of transition.

At present the following disadvantages are evident:

The large amount of material necessary to form a cylinder of sufficient size for determinations precludes the application of the method to rare materials.

The field of use is practically limited to powdered materials.

Determinations with the present procedure are accurate to ± 5 per cent. Refinements may increase the accuracy, but it is doubtful if the method could ever be called precise.

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